The role of abiotic and biotic mechanisms controlling the dynamics of the dissolved organic matter in pelagic ecosystem (NW Mediterranean)

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Doctoral Thesis
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By

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Ce n’est pas le plus fort de l’espèce qui survit, ni le plus intelligent.
C’est celui qui sait le mieux s’adapter au changement.

(Charles Darwin)

Summary

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PREFACE

Cette étude est une approche pluridisciplinaire qui m'a permis d'acquérir des connaissances et des compétences sur les processus biogéochimiques impliqués dans le fonctionnement des écosystèmes marins, en particulier, ceux qui affectent la dynamique de la matière organique dissoute. Une approche couplée entre des sorties en mer, régulières et un travail de laboratoire approfondi a été effectuée.

Ce travail de recherche s'est inscrit dans les programmes scientifiques MERMEX[1] du chantier MISTRALS[2] (projets nationaux français) et plus précisément dans le WP1 (programme DeWEX[3]), mais également dans le programme DOREMI[4] (projet sous l'égide du ministère espagnol des Sciences et de l'innovation, ICM-CSIC[5]). Au cours de mon travail, j'ai mis au point et développé pour le LOMIC (Laboratoire d'Océanographie Microbienne), les techniques d'analyses et des traitements de la matière organique dissoute colorée (CDOM) et fluorescente (FDOM), méthodes qui viennent compléter l'expertise reconnue de l'équipe sur le compartiment organique dissous (MOD). Ce travail a été possible grâce notamment à l'étroite collaboration avec le Dr. Cèlia Marrasé (CSIC).

Au cours de ma thèse, j'ai pu acquérir de solides compétences du travail à la mer grâce à une participation active à deux campagnes océanographiques hauturiers (DeWEX) et (MIFASOL). Pour la campagne DeWEX, j'ai passé 21 jours en mer et je me suis occupée des prélèvements, des filtrations et du conditionnement des échantillons (CDOM/FDOM, MOD, sels nutritifs dont ammonium et pigments). Il s'agissait d'un travail d'équipe, avec Louise Oriol et Tatiana Séverin du LOMIC, et Fayçal Kessouri (du LA). De retour au laboratoire, j'ai participé aux analyses du carbone organique dissous (COD) et particulaire (COP), en collaboration avec Mireille Pujo-Pay et Jocelyne Caparros.

Au cours de la campagne MIFASOL, j'ai passé sept jours en mer, pour la préparation et le conditionnement des échantillons de carbone organique total et dissous en collaboration avec Marín Isabel, Nunes Sdena et Rodriguez Caterina (doctorantes au CSIC). J'étais de plus responsable des analyses des propriétés optiques de la matière organique dissoute.

Finalement, j'ai eu également l'opportunité de participer à d'autres projets, comme le projet de campagne en mer CASCADE (MERMEX WP3 – Mars 2011) pour lequel j'ai fait les analyses et traitements des pigments par HPLC sur la plateforme de l'OOB dirigée par Karine Escoubeyrou, mais aussi le programme SPECIMed (Programme MISTRALS-WP2) pour lequel j'ai fait les comptages et l'identification des groupes taxomomiques du phytoplancton par microscopie inverse, ou encore le projet Vermeillecotox (CNRS - Région - AMP) pour lequel mensuellement (entre Avril 2012 et Avril 2013) j'ai fait des sorties journaliers en mer. Je me suis également impliquée dans les travaux en mer hebdomadaires et mensuels du service d'observation du laboratoire.

[1]MERMEX (Marine Ecosystems Response in the Mediterranean Experiment ; http://mermex.pytheas.univ-amu.fr).
[2]MISTRALS (Mediterranean Integrated Studies at Regional And Local Scales, http://www.mistrals-home.org/spip/).
[3]DeWEX (Deep Water Formation Experiment ; http://mermex.pytheas.univ-amu.fr/wp-content/uploads/2012/05/).
[4]DOREMI (Dissolved Organic Matter Remineralisation in the Ocean : Microbial and Biogeochemical Constraints).
[5]ICM-CSIC (Intitut de Ciències del Mar-Consejo Superior de Investigaciones Cientificas; http://www.icm.csic.es).

Glossary of relevent terms

a_{CDOM} (254)	Absorption coefficent at 254 nm (in nm)
a^*_{CDOM}(254)	Specific absorption coefficent of CDOM at 254 nm
CDOM	Chomophoric organic matter
Chl *a*	Chlorophyll *a*
CV	Coefficient of variation
CO	Carbon monoxide
CO_2	Carbon dioxide
DIN	Dissolved inorganic nitrogen
DIP	Dissolved inorganic phosphorus
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DWF	Dense Water Formation
EEM	Excitation-Emission Matrix
FDOM	Fluorescence organic matter
HMW	High Molecular Weight
H_4SiO_4	Silicate
LMW	Low Molecular Weight
LIW	Levantine Intermediate Water
MAW	Modified Atlantic Water
MLD	Mixing Layer Depth
NH^+_4	Ammonium
NO^-_3	Nitrate
OM	Organic Matter

Peak-A	FDOM at Ex/Em 260 nm/435 nm
Peak-C	FDOM at Ex/Em 340 nm/440 nm
Peak-M	FDOM at Ex/Em 320 nm/ 410 nm
Peak- T	FDOM at Ex/Em 280 nm/350 nm
POC	Particulate organic carbon
PON	Particulate nitrogen
POM	Particulate organic matter
PO^{-3}_4	Phosphate
QSU	Quinine sulfate units
S	Salinity
S_{CDOM}	Spectral slope
T	Temperature
ϕ (340)	Fluorescent quantum yield at 340 nm
UML	Upper mixing layer
UV-R	Ultraviolet Radiation
WMDW	Western Mediterranean Deep Water

CHAPTER I

INTRODUCTION AND OBJECTIVES OF THESIS

1. INTRODUCTION

1.1. Marine dissolved organic matter in the ocean

Marine dissolved organic matter (marine DOM) represents one of the largest exchangeable organic reservoirs at the earth's surface where it plays a essential role in the biogeochemical processes (mainly, in those related to the carbon cycle) since constitutes the main substrate to the heterotrophic microbial populations (Hedges, 2002, Hansell et al., 2009). A substantial part of DOM in the photic zone is labile and has been generated by biological processes, such as phytoplankton exudation, excretion by zooplankton, viral lysis, and sloppy feeding (Myklestad, 2000). Most of this DOM produced in surface waters is considered as labile (LDOM), that means that it could be quickly consumed by the heterotrophic osmotrophs to the extend that trophic condition allows it (Carlson & Hansell, 2015). This rapid DOM assimilation contributes to the mineralization of carbon and nutrients and to the production of refractory DOM (RDOM). This RDOM has very low turnover rates (Hopkinson & Vallino, 2005) and tends to accumulate in deep waters. The hal-life of RDOM could vary over a continuum from molecules with half-life of 50-10 years to molecules of 1000 years (see below for carbon). The diverse microbial activities that participate in the generation of recalcitrant organic compounds are part of the conceptual scheme for the microbial carbon pump (MCP) proposed by Jiao and coauthors, 2010. The MCP together with the organic carbon and the carbonate pump compose the biological pump by which CO_2 is pumped from surface to the deep ocean thanks to biological activities (Ridgwell & Arndt, 2015). The MCP involves bacteria, archea and virus that transform LDOM into RDOM, which is stored mostly in the deep ocean. The MCP operates in the whole water column independently of depth, sequestering carbon from the layer surface to the deep sea (Fig. 1).

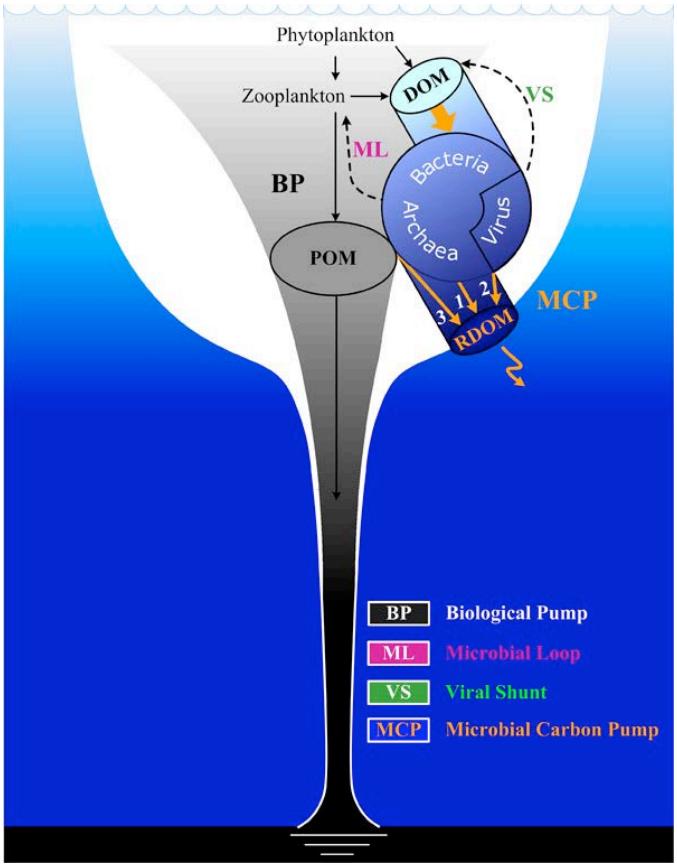


Figure.1. The major processes involving the carbon pump such as: Biological Carbon Pump and Microbial Carbon Pump (Jiao et al., 2010).

1.2. Marine dissolved organic matter in the carbon cycle

The marine dissolved organic matter expressed as dissolved organic carbon (DOC) constitutes a stock of 662 ± 32 PgC exceeding the inventory of organic particles in the seawater (Hansell et al., 2009). This quantity is comparable with all living vegetation in the Earth's continents (600 PgC) and with the CO_2 accumulated in the atmosphere (720 PgC, Hedges et al.,1992; Hedges, 2002). These quantity account for the largest bio-reactive pool of carbon in the ocean (Hansell & Carlson, 1998; Hansell et al., 2009; Jiao et al., 2010).

In the organic carbon pump, the CO_2 is fixed by the photosynthesis in organic carbon (dissolved and particulate) thanks to the light and dissolved inorganic nutrients used by the phytoplankton (Ridgwell & Arndt, 2015). It has been reported

that this organic carbon is produced at a rate of about 50 $PgCy^{-1}$ and is the base of the marine food web (Chisholm, 2000). A large part of this carbon (~ 39 $PgCy^{-1}$) is respired by organisms in surface waters and converted back to CO_2 and released to the atmosphere (Chisholm, 2000; Hansell et al., 2009), and only 11 $PgCy^{-1}$ is sinking inward, where it is partially oxidized by heterotrophic respiration (Laws et al., 2000). Yet, geochemical models estimated that about 20% of the annual net carbon production (1.9 PgC) is exported as DOC to depths >100 m (Hansell et al., 2009), while the carbon export in particulate form is of about 9.6 $PgCy^{-1}$. However only small portion of these fractions will reach bathypelagic waters (0.2 and 2.3 $PgCy^{-1}$ for dissolved and particulate fractions respectively). See Figure 2.

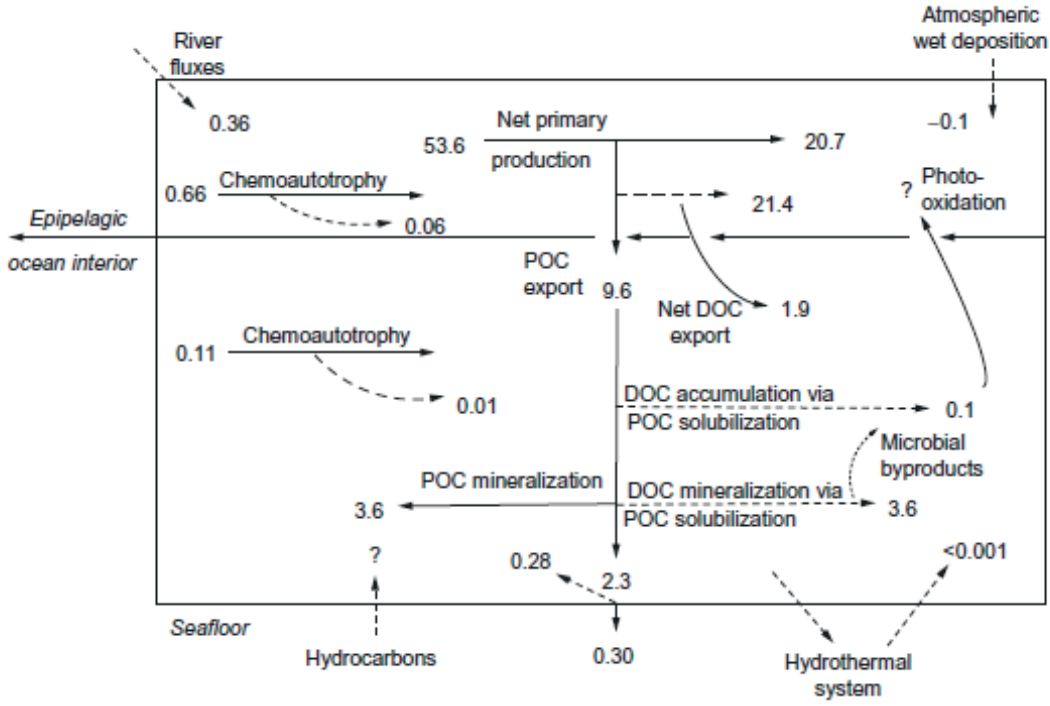


Figure. 2**.** Scheme of the global budget (PgC y^{-1}). Solid lines indicate particulate, while dashed lines indicate dissolved organic matter. The carbon pools area assumed at steady state; all input fluxes (value at origin of arrow) are balanced by removal (value at the end of the arrow). Question marks indicate figures with high uncertainty. (from Carlson & Hansell, 2015).

The carbonate pump involves the production and dissolution of calcium carbonate ($CaCO_3$) by marine organisms (e.g. coccolithophores, foraminifera and pteropods) and its following transport to depth. With this mechanism, the particulate organic carbon (POC) produced by phytoplankton during photosynthesis and formed in the surface ocean (with the following chemical reaction associated: $Ca^{2+}_{(aq)} + 2\ HCO_3^-{}_{(aq)} \leftrightarrows CaCO_3 + CO_2$) is transported to the depth sea (Jansen, 2001). When organisms die their carbonate skeletons are transported to seabed, $CaCO_3$ dissolution occurs during this transport (Elderfield, 2002). The $CaCO_3$ dissolution tends to increases carbonate and bicarbonate ions lowering atmospheric CO_2 in upwelling regions (Sigman & Boyle, 2000). In addition it has been estimated that more than 50% carbonate is dissolved in the water column (~ 0.5 $PgCaCO_3y^{-1}$; Feely et al., 2004), the remainder reaches the sediments and only 20% is buried in shallow and deep sediment (Ridgwell & Arndt, 2015).

The bio-reactivity of the DOC pool refers to the chemical structure and to the residence time of the different compounds. Considering these particularities, Hansell in a recent review (2013) described five major fractions in the ocean, which are illustrated in the Fig. 3: labile, semi-labile, semi-refractory, refractory and ultra-refractory dissolved organic matter (LDOC, SLDOC, SRDOC and RDOC respectively). LDOC, representing only a small fraction (< 0.2Pg) of the DOC inventory, is quickly assimilated by the marine microorganisms and it supports the metabolic energy and the nutrients demand by heterotrophic prokaryotes (Carlson & Hansell, 2015). The LDOC fraction comprise organic acids, organic phosphorous, sulfur compounds, lipids, amino acids and monosaccharaides, as well as hydrolysable high molecular weight (HMW) compounds (Amon & Benner, 1994; Benner, 2002). It has been estimated that LDOC production rate is ~15-25$PgCy^{-1}$ in the photic zone, and its residence time of hours to days (Fig. 3b, Carlson & Hansell, 2015). The SLDOC is dominated by a family of carbohydrates with spectroscopic and chemical properties throughout the global ocean (Aluwihare et al., 1997). This fraction is more resistant than LDOC to microbial degradation, thus it can persist for months to years (Fig. 3b, Carlson, 2002), and it is considered as exportable from the euphotic zone to deeper layers (Nagata, 2008). Recent studies have estimated that its global inventory is sustained at ~6±2PgC, with a production rate of ~3.4$PgCy^{-1}$ (Hansell et al., 2012; Hansell, 2013). The SRDOC constitutes an inventory of about

14 PgC and its accumulation in the upper-layer requires a permanent pycnocline. The RDOC, is resistant to biological decomposition and dominates the organic matter pool in deep waters (about 630 PgC), being its residence time of a scale of millennia, in a range of 4,000 to 16,000 years (Bauer, 2002; Hansell, 2013). Finally, the URDOC is a small fraction of RDOC (~ 2%) and this part has been inferred from radiocarbon and molecular composition analyses (Dittmar & Koch 2006; Dittmar & Paeng, 2009; Ziolkowski & Druffel, 2010). Lifetime of this fraction can be larger than 40000 years.

A recent study based on experimental evidences proposed an alternative mechanism for the long-term storage of labile DOC in the deep ocean (Arrieta et al., 2015). According to these authors, deep-water DOC consists of many different, intrinsically labile compounds at concentrations too low to compensate the metabolic costs associated to their utilization (as previously suggested by Komarova-Komar & Egli, 1985; Jannasch, 1995).

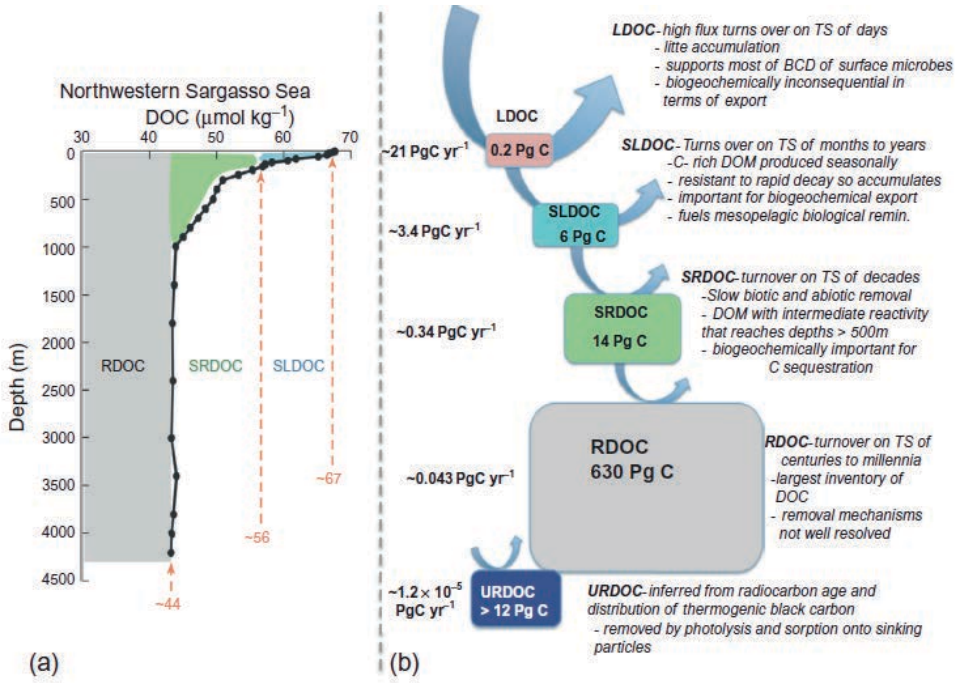


Figure. 3. (a) Vertical distribution of DOC fractions in the water column defined by its reactivity. (b) Estimated range of DOC concentrations for the different DOM pools observed in stratified oligotrophic waters. Estimated inventories (in box) and removal rates (figures to left of box) for the different fractions (from Carlson and Hansell, 2015).

2. Optically active fractions of DOM

Some compounds of the marine RDOM category have optical properties and absorb light (UV and visible) and part of these compounds can emit fluorescence. For this reason, colored and fluorescent dissolved organic matter have been used as proxies of RDOC to study the distribution of recalcitrant organic matter (Yamashita & Tanoue, 2008; Jørgersen et al., 2011; De La Fuente et al., 2014; Catalá et al., 2015).

2.1. Fundamentals of absorption and fluorescence of DOM

Light absorption by a chromophore is characterized by its nature and its intensity according to the Beer-Lambert law. The light absorption depends upon electronic transitions of energy levels of the atoms in the sample (Stedmon & Nelson, 2015). In the UV-R and visible region, these transitions involve electrons type π-double, triple or rings aromatics, which have states of vibrational and rotational electronic energy and therefore specific absorptivity (Repeta, 2015). Therefore, the Beer-Lambert law explains that when the energy absorption of a photon coincides exactly with the difference between the ground state (S_0) and the excited state (S_1 or S_2), the outermost electrons can jump to another empty orbital (S_0) of higher energy level (S_1 or S_2). Once that electron is excited, it emits radiation and subsequently returns to its ground state after have lost energy to molecular vibration and internal conversion (not radioactive process) (Stedmon & Nelson, 2015). These processes are illustrated in the Fig. 4.

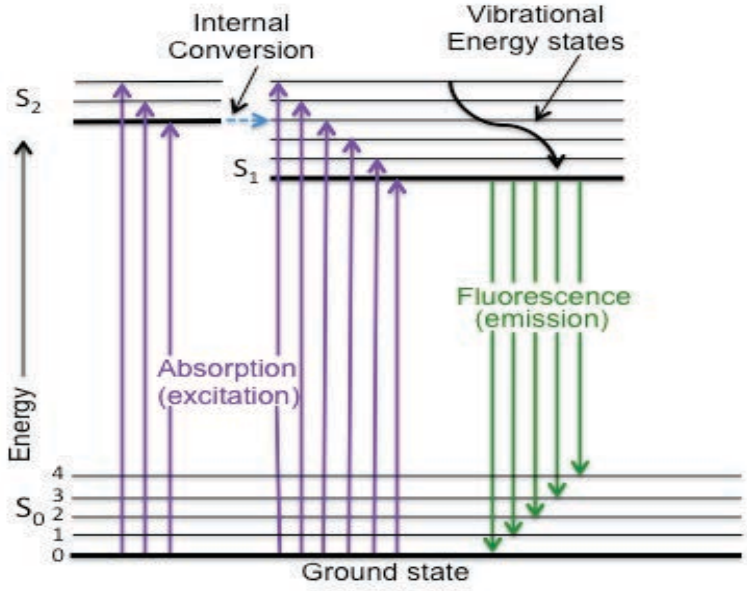


Figure. 4**.** Jablonski diagram typically, S_0, S_1, and S_2 are singlet group, first and second electronic states of flourophores respectively. 0, 1, 2, etc. indicates number of vibrational energy levels shown the principles of the absorption and fluorescence (from Lakowicz, 2006).

2.2. Absorption of CDOM

Chromophoric dissolved organic matter (CDOM) is an important component of DOM pool in the ocean, and play an essential role in the carbon cycle (Coble, 1998).

This fraction of DOM is optically active and measurable in natural seawater. Its analysis is efficent, sensible, fast, not expensive, and requires only a small volume of sample. It can represents about 20 % of DOC in open ocean and close to 70% in coastal zones (Siegel et al., 2002; Coble, 2007).

CDOM controls the penetration of light energy in the water column, absorbing in the UV-R (200-400 nm) and visible (400-800 nm) radiations of spectrum (Jerlov, 1976; Kirk, 1994). This control gives rise to ecological implications. First, CDOM can limit the light available for photosynthesis, causing a decrease in primary production (Arrigo & Brown, 1996; Morris & Hargreaves, 1997; Conde et al., 2000; De Mora et al., 2000; Kuwahara et al., 2000). The second, CDOM can reduce harmful UV-R effects on plankton organisms, acting as a photo-protector (Williamson et al., 2001).

CDOM can play a substantial role in the biogeochemistry of natural waters through its light reactivity (Conde et al., 2000; Stedmon & Nelson, 2015), which include the photo-oxidative degradation of organic matter, photochemical production of trace gases (e.g. CO_2, CO), absorption inorganic constituents (nitrate, nitrite and sulfide) and photochemical production of lower molecular weight (LMW) organic compounds (Blough & Del Vecchio, 2002). Furthermore, CDOM also interferes in satellite-derived chlorophyll measurements (Carder et al., 1989; Vodacek & Blough, 1997). For all these reasons, its study has increased in the past two decades.

The absorption spectra of CDOM are not structured, but the complex mixture of chromophores typically decreases exponentially with wavelength (Blough & Del Vecchio, 2002, Eq. (1)):

$$a_{CDOM}(\lambda) = a(\lambda_0)e^{-S(\lambda - \lambda 0)} \quad (1)$$

Where a(λ) and a(λ_0) are the absorption coefficients at wavelength (λ) and reference wavelength (λ_0) respectively and *S* is spectral slope (Bricaud et al., 1981; Carder et al., 1989; Green & Blough, 1994). The absorption coefficient at a particular λ is obtained according to Eq. (2):

$$a_{CDOM}(\lambda) = 2.303A(\lambda_{250-700})/L \quad (2)$$

Where a(λ) is the absorbance (log I_0/I, dimensionless), *l* is optical path length (m or cm) and 2.303 is a factor, that allows the passage of napierian logarithm to decimal logarithm (Fig. 5). The spectral slope was calculated over wavelength range ($S_{250-500}$ and $S_{275-295}$) using linear regressions of the natural log-transformed $a_{CDOM}(\lambda)$ according to Nelson et al. (2004) and Helms et al. (2008).

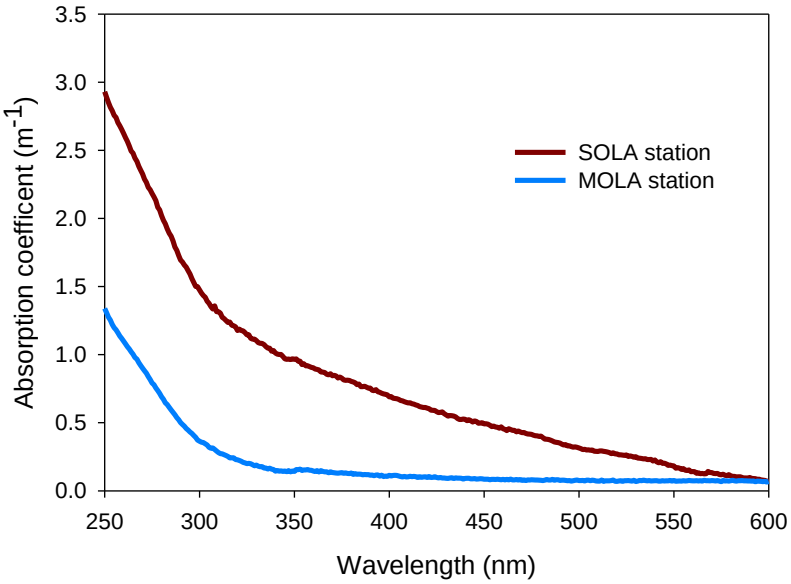


Figure. 5. Typical absorption coefficient of surface Mediterranean Sea water. Brown line represents a coastal station (SOLA) and blue line an offshore station (MOLA). Measures for this figure were determined in February 2013.

The value of absorption coefficient independent of the wavelength provides relevant information about quantity of CDOM in the sample. Values of $a_{CDOM}(340)$ in aquatic systems varied depending on the area studied, for exemple in the Ria de Vigo values of 0.40 ± 0.17 m^{-1} have been reported by Romera-Castillo et al., 2011, while, higher values (0.81± 0.18 m^{-1}) have been found in the Bay of Banyuls-sur-mer (Sanchez-Perez et al. *in preparation*, see chapter 3).

In addition, the value of spectral slope (S_{CDOM}) can be used as a descriptor of the origin of CDOM. In fact, low values (S < 0.018 m^{-1}) in coastal zones have been related to the terrestrial organic mater (OM). Indeed, this OM is characterized by aromatic compounds of high weight molecular (HMW) and high reactivity (Opsahl & Benner, 1997), which explain a high absorption in low part of the spectrum. On the opposite, high values (S > 0.018 m^{-1}) for oceanic systems, are attributed to “marine” OM, e.g. autochthonous and/or photo-bleached origin (Blough & Del Vecchio, 2002). The spectral slope is also considered as a proxy for molecular structure of CDOM, when its aromatic content and its molecular weight increase, the S_{CDOM} presents low values. This decrease is due, in part, to the presence of a set of

different chromophores with extended aromatic system, which absorbs at long wavelengths; otherwise, this increment in absorption at long wavelengths could come from intermolecular charge transfer transitions between chromophores of high aromaticity (Power & Langford, 1988; Blough & Green, 1995). Conversely, an increase of S_{CDOM} suggests a loss of aromaticity and a decrease in the average molecular weight of CDOM. In fact, Vodacek & Blough, (1997) and Moran (2000), reported that photo-degradation process can produce the same effects, which largely complex the interpretation of S_{CDOM} measurements.

In summary, both absorption coefficent and spectral slopes can be used as proxies to some characteristics of the molecular structure of CDOM. For exemple, specific absorption coefficent at 254 nm [$a^*_{CDOM}(254)$] is used as aromaticy index (Weishaar et al., 2003).

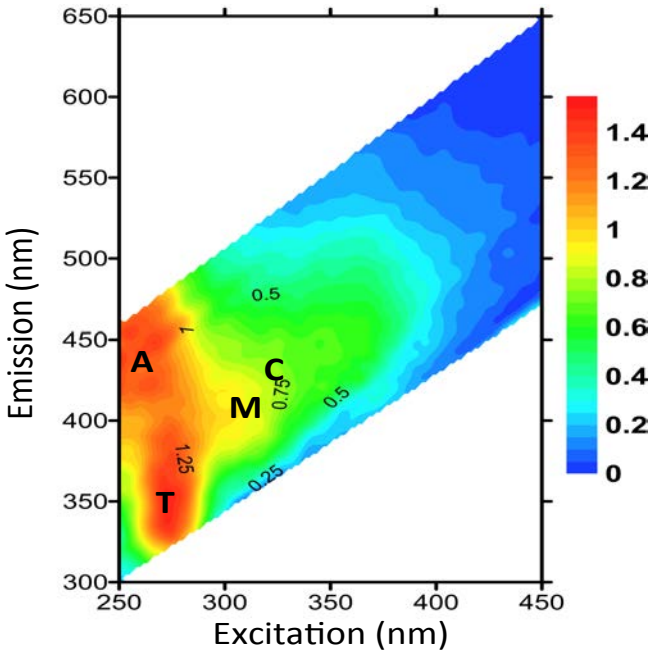
2.3. Fluorescence of DOM

A small fraction of CDOM can emit blue fluorescence when excited by UV-R, which is called fluorescent dissolved organic matter (FDOM; Coble, 1996, 2007). In earliest studies, this fraction was used as a tracer of riverine input of DOC in the coastal waters (Kalle, 1949; Duursma, 1974). However, FDOM in oceanic environments has been investigated using fluorescence spectroscopy analyses, and, in particular, Excitation-Emission Matrices (EEMs) have been applied to understand the dynamics of DOM (Blough & Del Vecchio, 2002; Nieto-Cid et al., 2006; Romera-Castillo et al., 2010). EEMs are obtained by collection of multiple emission spectra at different excitation wavelength represented in 3D, which provides the presence of fluorophores and its relative concentration in the sample.

Two main groups of fluorophores have been identified depending of their excitation and emission couple (Ex/Em): First group is composed of protein-like substances. This group exhibits two major types of aromatic amino acids such as tryptophan and tyrosine which, have fluorescence maxima at Ex/Em 280 /350 nm (Peak-T), and Ex/Em 275 /300 nm (peak-B) respectively (Coble, 2007). Peak-T has been considered as a significant tracer for labile DOM (Coble, 1996; Determann et al., 1996; Yamashita & Tanoue, 2003; Nieto-Cid et al., 2006). The second group is associated with humic-like compounds, commonly known as Peak-A (Ex/Em

250/435 nm), Peak-C (Ex/Em 340/440 nm) and Peak-M (Ex/Em 320/410 nm). All these peaks can be visualized in the excitation-emission matrices (EEMs; Fig. 6). Both Peak-C and Peak-M (terrestrial and marine humic-like respectively) have been found in fresh-water and marine environments.

Coble (1996) reported that humic-like peaks in freshwater samples presented a shift to longer wavelengths. This shift is due to terrestrial humic-like substances which are more aromatic compounds that marine humic-like substances (Benner, 2003). Both peaks M and C have been considered photo-degradable but rather resistant to bacterial degradation and they have been associated with catabolic microbial activities (Nieto-Cid et al., 2006; Romera-Castillo et al., 2010). Furthermore, other authors (Chen & Bada, 1992; Jiao et al., 2010) observed that these peaks can accumulate in the ocean for long time scales when they are not exposed to natural UV-R, allowing the sequestration of anthropogenic CO_2 in DOM.



Fiigure. 6. Typical Excitation-Emission Matrix of a surface Mediterranean seawater expressed in quinine sulfate units (QSU). Characters indicate the location of the main fluorescence peaks: A, C, M and T. EEM was collected at SOLA station at 3 m depth on February 2, 2013.

The EEMs matrices have been typically used for some decades, because contain considerable information in the fluorescent properties of DOM (e.g. Fig. 6). This information can be used as a fingerprint that permits identify the origin and fate of the CDOM (Table I). For more objective data interpretation, multivariate analysis methodologies have been recently adapted to analyze the information contained in the EEMs (Stedmon et al., 2003; Boehme et al., 2004). These analyses include principal component analysis (PCA) and parallel factor analysis (PARAFAC), which provide information on excitation-emission spectra of individual components (Stedmon & Bro, 2008).

In summary, both absorbance and fluorescence provide important information about the quality (flourophores identification, e.g. humics and/or proteins-like substances) and quantity (fluorescence intensity), of the optically active compounds, and they can be used as indicators of OM origin (allochthonous/ autochthonous), and of possible biotic and abiotic mediated transformations.

Table I. Fluorescent components identified in aquatic systems (Coble et al., 1998, 2007).

Fluorescence DOM	**Excitation λ (nm)**	**Emission λ (nm)**
Peak-A (humic-like)	250	435
Peak-M (marine humic-like)	320	410
Peak-C (terrestrial humic-like)	340	440
Peak-T (protein-like)	280	350
Peak-B (tyrosine)	275	300

3. Distribution, sinks and sources of CDOM

3.1. Distribution in the ocean

The distribution of CDOM in the ocean is mainly driven by physical processes such as vertical mixing, turbulence, up-and/or down-welling of water masses, lateral advection and by photo-degradation processes (Helms et al., 2013; Yamashita et al., 2013). In surface waters CDOM distribution can show apparently similar patterns than that of the chlorophyll (Siegel et al., 2002). Briefly, CDOM tends to decline with distance from the coast (Stedmon & Nelson, 2015) as the main sources are continental, and with depth because microbes are also the major producers. In surface waters, high values of CDOM have been registered in subarctic zones (a_{CDOM} (325) > 0.17 m^{-1}), low values in the sub-tropical gyres (< 0.05 m^{-1}) and intermediate values in Equatorial upwelling region and Southern Ocean (about 0.1-0.15 m^{-1}, Nelson et al., 2010), while, the deep North Pacific and North Indian oceans shown a greater vertical gradient of CDOM across the main thermocline (~ 0.22 m^{-1}) that it is the Atlantic basin (Fig. 7, Nelson et al., 2010).

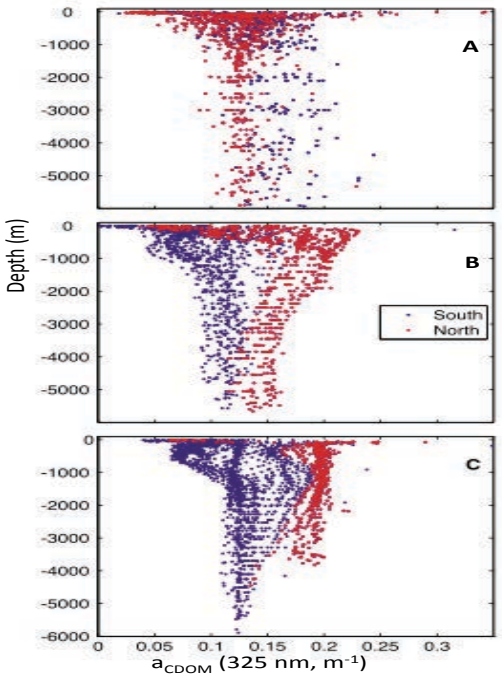


Figure 7. Exemple of CDOM absorption coefficient at 325 nm (m^{-1}). Blue and red symbols represent observations south and north of the Equator respectively. A) Atlantic Ocean, B) Pacific Ocean, and C) Indian Ocean (from Nelson et al., 2010).

3.2. Sinks and sources of CDOM

In the coastal areas influenced by river discharges, the main source of CDOM is of terrestrial origin. This terrestrial material represents only ~ 2-3% of total organic matter in the ocean (Opsahl & Benner, 1997) that is characterized by a high content of humic and fulvic substances, which have high aromaticity and high molecular weight. However, in the open ocean, the dominant source of CDOM is the "i*n situ*" production, which accounts for more 95% of total CDOM, and is produced by a variety of mechanisms. The *in situ* production of CDOM has been mostly associated to prokaryotic activities, however some studies pointed out that eukaryotic organism can also mediate the CDOM production. For example, CDOM concentration increases with grazing activities (Toulen & Arvola, 2012). In the same way, the FDOM production by phytoplankton and posterior transformations by prokaryotic cells has been described using experimental approaches by Romera-Castillo et al. (2010, 2011). These authors found that the growth of different phytoplankton species can induce the increase of different fluorescent substances. Field studies have also associated chlorophyll variability with CDOM distributions (Vodacek & Blough, 1997; Siegel et al., 2002; Xing et al., 2014).

The main sink of CDOM is photo-bleaching, a key process to consider when examining the dynamics of DOM in aquatic systems (Moran et al., 2000). Therefore, changes in DOM composition resulting from exposure to solar radiation include loss of absorbance capacity and fluorescence efficacy, production of biologically labile compounds. The main sources and sinks of CDOM shown in Figure 8.

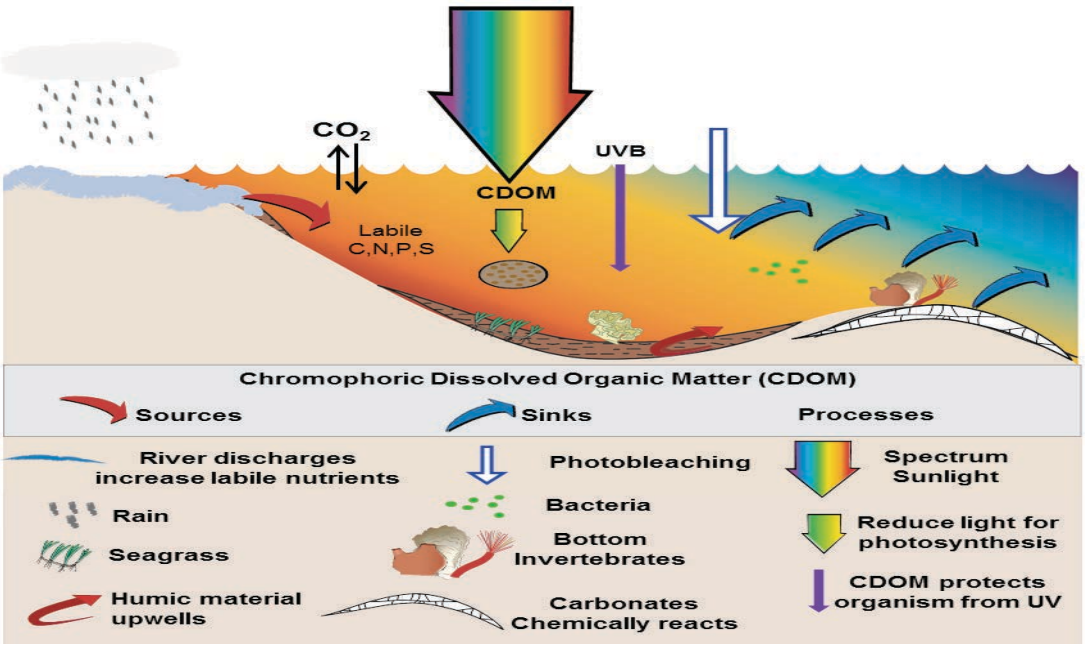


Figure 8. Schematic diagram of sources, sinks and processes of CDOM in the aquatics systems (redrawn from Beever, 2007).

4. STUDY AREA (Mediterranean Sea)

4.1. General context of the Mediterranean Sea

The Mediterranean Sea is large semi-enclosed basin, with a surface area of $2.5 \cdot 10^6$ km^2 and $46 \cdot 10^3$ Km of coastline (Santinelli, 2015) and is surrounded by three contrasted continents (Europe, Asia and Africa). Its smaller inertia due to relative short ventilation and residence time of its water masses ~ 70 years when compared to 200-1000 years for the others oceans (Falkoswki et al., 1998); makes it highly reactive to external forcings and it can be considered as a “hotspot” for climate change. Moreover, natural perturbations interact with the increasing demographic and economic developments occurring heterogeneously in the coastal zone.

The Mediterranean Sea is classified as a moderate oligotrophic basin with relatively low nutrients concentrations (McGill, 1965; Krom et al.,1991) compared with other oceans (Estrada et al., 1999). It is characterized by an important west-to-east gradient of chlorophyll distribution, with an extremely oligotrophic Eastern basin and a more productive Western side (D’Ortenzio & Ribera d’Alcala 2009, Pujo-Pay et al., 2011), indicating that the Mediterranean sub-regions have asymmetric physical, chemical and biological forcing factors (as suggested, Crispi et al., 2001). Superimposed to these longitudinal differences, a pronounced biological heterogeneity is also observed in areas hosting deep convection, fronts, cyclonic and anti-cyclonic gyres or eddies (Robinson et al., 2001). In such areas, the intermittent nutrients enrichment promotes a switching between a small-sized microbial community and diatom-dominated populations (Siokou-Frangou et al., 2010). A coupled observation/ modelling study performed by Crise et al. (1999) shows that the biogeochemical response of ecosystems to change in trophic type ("oligo- vs meso- trophisation") may depend on changes in export of organic matter to the aphotic layers, which mainly depends on vortices/ filament structures (meso- submesoscale space) and/or on the blooms intensity (location/scale and timescale). These findings were confirmed and extended to the whole Mediterranean Sea by the works of Pujo-Pay et al. (2011).

It has been widely reported that the nutriens availability in the Mediterranean Sea is controlled mainly, by physical (e.g. mixed layer evolution) and biological (e.g. production/ consumption/ mineralization) processes, but interestingly, in the NWM the

severe winds bring in winter cold and dry continental air over the warmer ocean, generating intense air-sea heat exchanges and surface waters cooling (Flamant & Pelon, 2003). The loss of heat and buoyancy and mixing mechanisms induce dense water formation (DWF) during winter and early spring, and may trigger deep ocean convection (Marshall & Schott 1999). This process, although relatively local, strongly impacts the macronutrients distribution of the whole basin (Béthoux et al., 2002) and it is one of the main forcing factors of the spring bloom observed in the area. In fact, Marty & Chiaverini (2010) reported that in the Ligurian Sea that, in winter, nitrate concentration can vary threefold depending of the intensity of the convection, indicating a strong relation between the depth reached by wintertime convection and the nutrient enrichment of the surface layer. The nutrient enrichment triggers short and intense diatom production and deep vertical flux in winter before the onset of the stratification and the regular spring bloom (Stemmann et al., 2002; Marty & Chiaverini, 2010).

4.2 Nutrients inputs into the Mediterranean Sea

In the Mediterranean basin, the inputs of nutrients at the boundaries (e.g. exchanges through straits, river discharges, wet and dry atmospheric deposition) are particularly relevant (Pujo-Pay et al., 2006, Durrieu de Madron et al., 2009). Furthermore, extreme events (e.g. large river floods, Saharan dust deposits, deep water formation) are recurrently observed (MerMeX Group, 2011), inducing a strong variability in terms of quantity and quality of the spatio-temporal nutrients repartition. However, the relative importance of the different sources in relation to the estimated nutrient budgets at a regional scale, as well as their seasonal variability, are still poorly documented (UNEP-MAP 2003, Schroeder et al., 2010). The extreme events, in particular, atmospheric depositions also affect the composition of DOM in terms of elemental stoichiometry in all compartments (particulate and dissolved, inorganic and organic). In fact, it has been reported changes in ocean biogeochemistry such as: an excess of carbon, a deficiency of phosphorus relative to nitrogen and a sporadic deficiency of silicate have been reported by Béthoux et al. (2002).

Although atmospheric deposition has been recognized since long time ago (e.g. Guerzoni et al., 1997; Bonnet et al., 2006; Guieu et al., 2010; Guieu et al., 2014), scarce studies included the examination of optical properties of FDOM and the

relative importance of FDOM inputs in relation to the *in situ* concentration in Mediterranean waters.

4.3. Stations studied

The two main contrasted stations sampled in this work are part of the "Service d'Observation" of the laboratory since 1997 for the coastal one (SOLA; 42°29'300 N - 03°08'700 E) and since 2003 for the oceanic one (MOLA; 42°27'20 N – 03°32'565 E) and are located in the Gulf of Lion (Fig. 9).

The SOLA station is located 0.3 milles from the coast in the Bay of Banyuls on 27 m depth, and is characterized by a marked seasonal pattern (Salter et al., 2015). During winter, episodes of strong wind homogenize and cool the water column. Important rainfalls and continental inputs currently occur, favoring the renewal of nutrients and thus the activities of phytoplankton and bacteria. Indeed, from winter to early spring, blooms of picophytoplankton are frequently observed. In summer, the calm and warm period quickly isolates the surface water from nutrient sources and stratification rapidly reaches the bottom. This period is characterized by low phytoplankton and bacterial activities due to rapid nutrient depletion.

The situation in MOLA station at 19 milles offshore and 600 m depth is quite different (Laghdass et al., 2012). In winter, the station could be influenced by the formation of deep water, either by convection, or by cascading in the Lacaze-Duthier canyon and along the continental slope (Mermex Group, 2011). These processes, even if limited in intensity enriched the euphotic layer at the origin of a strong and well identified spring bloom (D'Ortenzio & Ribera, 2009). This bloom is followed by a stratification period, which allows the formation of Deep Chlorophyll Maximum (DCM) that deepens during summer with the evolution of the nutricline. Then, at the end of summer, a clear upper mixing layer (UML) characterized by low or undetectable nutrient concentrations and low biological activities are separated from the deep enriched water. During autumn, the UML progressively deepens under the influence of gust of winds.

Complementary to these field studies, we perfomed experiments with natural waters sampled in two permanent stations: the Barcelona coast (41^0 22' 30" N, 2^0 11' 59" E) and the Blanes Bay Microbial Observatory (41^0 40' 0" N, 2^0 48' 0" E) (Fig.9).

These two sites at a short distance in the Catalan coast (62 km) are similarly affected by climatologic events, however the Barcelona station is more influenced by anthropogenic activities (Romero et al., 2014). We also used the database of dust deposition compiled during the ADEPT project (ICM-CSIC) during 23 months (September 2012-July 2014).

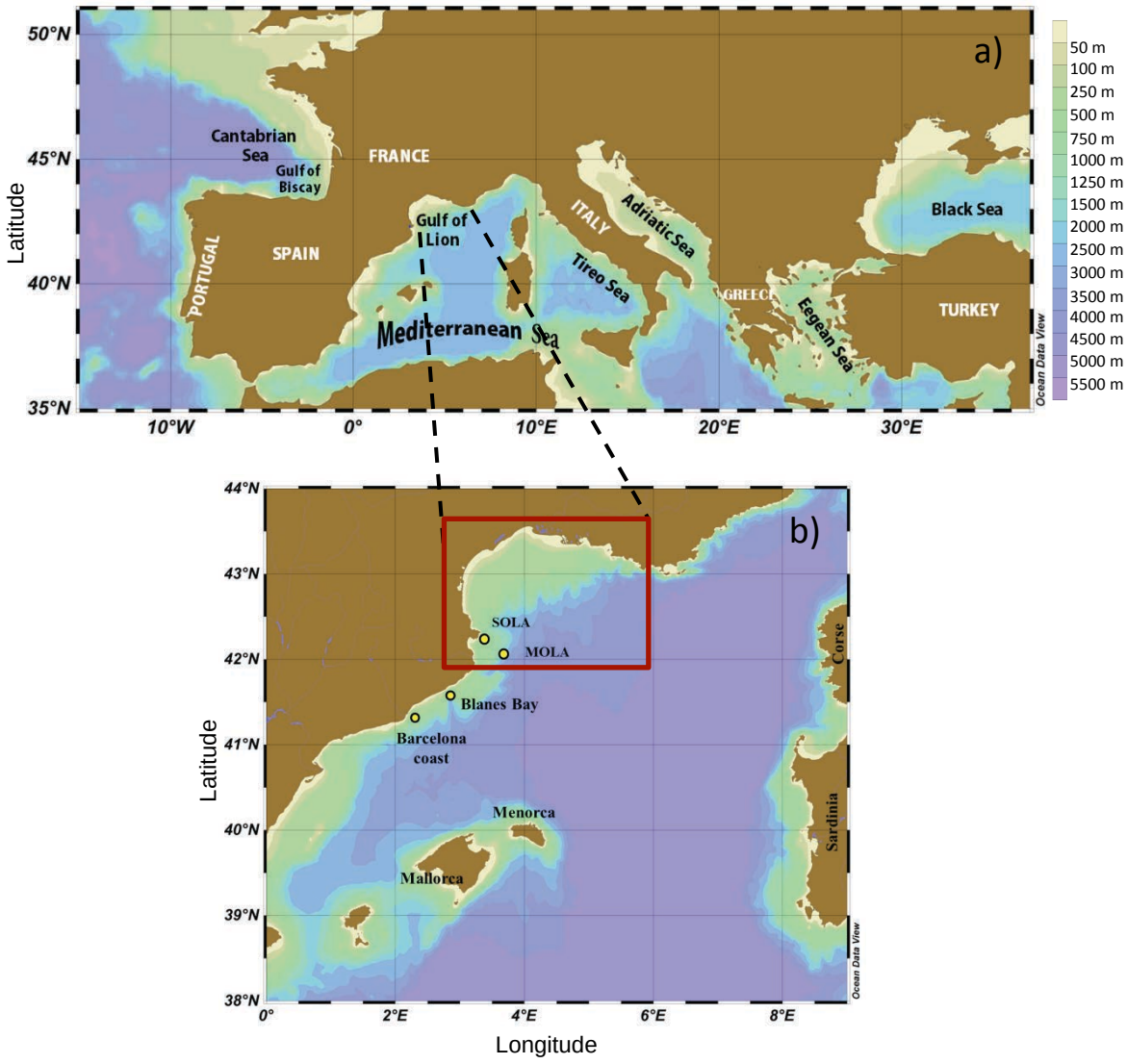


Figure 9. (a) General Mediterranean map. (b) Localization of the different sampling stations in this study, the red square corresponds to the Gulf of Lion area. The color scale indicates the bathymetry.

5. OBJECTIVES OF THESIS

This work is a contribution for the understanding of the dynamics of the DOM pool in marine pelagic ecosystems. By using the fluorescent properties of the CDOM samples from two time-series stations in coastal and offshore areas together with two experimental mesocosms, we aim to describe the seasonal variability of the DOM pool and to define the main drivers of the observed variability. Finally, the general aim of this thesis is to determine the influence of biotic (the equilibrium of autochthonous production and/or consumption by phytoplankton and prokaryotic organisms) and abiotic (e.g. solar radiation, land water inputs) processes on the DOM temporal and spatial (vertical) distribution in temperate marine systems. Before a general conclusion and perspectives (Chapter 5), the specific objectives are separated in 3 chapters as follow:

***Chapter 2*:** To identify the key environmental parameters which modify the quantity and quality of DOM in a coastal bay of the North Western Mediterranean Sea.

Sanchez et al. Coupled and mismatched temporal patterns of organic and inorganic nutrients in a NW Mediterranean coastal station. (In preparation)

Chapter 3: To analyze the temporal and vertical DOM variability through CDOM/FDOM optical properties in oceanic station of the North Western Mediterranean Sea in relation to biotic and abiotic factors during one year period. We also aim to evaluate this period in relation to a general context of global change thank to the observation time-series from 2007-2014 at the studied station.

Sanchez et al. Seasonal variability and characterization of the dissolved organic pool (CDOM/FDOM) at an offshore station (NW Mediterranean Sea) (In preparation).

Chapter 4: To identify the FDOM alterations induced by different types of dust (Anthropogenic and Saharan) and their possible effects on posterior biological-mediated transformations, as well as to evaluate the relative importance of atmospheric input in relation to the FDOM pool of surface waters in a coastal Mediterranean ecosystem (Barcelona coast and Blanes Bay Microbial Observatory).

Sanchez et al. Dust inputs affect the optical signatures of dissolved organic matter in NW Mediterranean coastal waters. (Submitted in Scientia Marina)

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CHAPTER II

COUPLED AND MISMATCHED TEMPORAL PATTERNS OF ORGANIC AND INORGANIC NUTRIENTS IN A NW MEDITERRANEAN COASTAL STATION

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ABSTRACT

The seasonality of diverse environmental parameters in coastal ecosystems is still a subject of debate. In temperate areas, episodic meteorological events introduce abrupt changes in littoral zones in comparison to open sea, where changes tend to be more gradual along the year. In addition, the inputs of nutrients and pollutants in coastal areas are strongly influenced by the anthropogenic activity on land, and those inputs do not necessarily follow seasonal trends. As a result, the study of the temporal variability in coastal systems requires high sampling frequency, often on the order of each week. In the present study, we used a weekly sampling scheme to examine the temporal variability in a coastal system. We examined the temporal trends of nutrients and autotrophic biomass for a period of 15 years (2000-2014). In addition, we, exhaustively, evaluate the fluctuation of different fractions of dissolved organic matter (DOM) from February 2013 to April 2014. During this period, two, extremely high, fresh water intrusions occurred in the study area, which influenced the dynamics of some fractions of DOM, particularly the humic-like fraction. Inorganic nutrients and Chlorophyll showed regular seasonal patterns, while DOM fractions did not follow a clear temporal trend. This is, probably, because factors like microbial activity and light exposure simultaneously affect the optical properties of DOM, but in opposite directions. Interestingly, dissolved organic carbon (DOC) exhibited the highest variability in summer, when the rest of parameters showed minimum variations. To explain this mismatch we propose a sequence of abiotic and biotic phenomena driving the DOC dynamics. In the suggested conceptual frame, the biological factors are dominant in the summer, while during the rest of the year; DOC dynamics depends strongly on episodic meteorological events.

Keywords: Chromophoric dissolved organic matter (CDOM), Fluorescent dissolved organic matter (FDOM), NW Mediterranean Sea, Coastal systems, Seasonality.

1. INTRODUCTION

Chromophoric dissolved organic matter (CDOM) is a major fraction of dissolved organic matter (DOM) that interacts directly and indirectly in biogeochemical cycles, principally in the carbon cycle. CDOM absorbs light over a broad range of ultraviolet (UV) and visible wavelengths and consequently it can shade plankton cells, thus reducing light for photosynthesis and preventing UV cell damage (Blough & Zepp, 1990).

In marine systems the dynamics of CDOM is governed by physical and biological processes, such as photobleaching or *in situ* microbial activity (Nelson & Siegel, 2002 ; Ortega-Retuerta et al., 2009; Romera-Castillo et al., 2013). This optically active component in oceanic regions could represent about 70 % of the total dissolved organic carbon (DOC) (Chen & Bada, 1992), and it has been demonstrated that this percentage can increase in areas with riverine influence (Blough & Del Vecchio 2002; Coble, 2007).

A small fraction of CDOM can emit fluorescence when excited by ultraviolet radiation, the so called fluorescent dissolved organic matter (FDOM; Coble, 1996, 2007). FDOM in aquatic systems has been characterized using fluorescence spectroscopy analyses and, in particular, measurements of Excitation-Emission Matrix (EEMs) have been applied to understand its dynamics (Blough & Del Vecchio 2002, Nieto-Cid et al., 2006, Romera-Castillo et al., 2010). Using EEMs matrices, Coble (1996) defined three types of substances: two of them humic-like: peak–M and peak–C; and the third one protein-like: peak–T.

Peak–M substances are considered mainly of *in situ* marine origin, rather bio-refractory and photo-labile, and their excitation/emission wavelength ranges are 312-320/380-410 nm (Coble 1996, Nieto-Cid et al., 2006), Peak–C substances emit at 420-480 nm when excited at 340-350 nm and are associated to materials of terrestrial origin and also to biological activity or catabolism of marine prokaryotes (Coble 1998; Romera-Castillo et al., 2011; De La Fuente et al., 2014). Peak–T compounds emit radiation in the wavelength at 350 nm when excited at 280 nm and might be considered as a tracer for labile DOM (Yamashita & Tanoue 2003).

The optical properties of the CDOM provide information of the chemical structure and biogeochemical processes of DOM in aquatic environments (e.g. Green & Blough, 1994). The ratio of a_{CDOM} with respect to DOC concentration gives us the specific absorption coefficient, $a^*_{CDOM}(254)$ that has been used as a proxy for aromaticity (Weishaar et al., 2003), and the ratio between the emitted fluorescence and the absorption at 340 nm ($a_{CDOM}(340)$) provides the quantum yield at 340 nm (Φ340), which is an indicator of degradation processes (De Haan, 1993).

CDOM monitoring in Mediterranean coastal areas has shown different temporal patterns, which go from weak to strong seasonality (Para et al., 2010; Romera-Castillo et al., 2013). Such high variability in the temporal trends of coastal systems has been also pointed out in relation to plankton dynamics (Cloern & Jassby 2008; Romero et al., 2014), and makes it difficult to predict the system response to future conditions. To better understand the temporal variability and the role of the CDOM in aquatic systems, we, here, present a 14-month dataset of weekly samplings in the SOLA station, in the Bay of Banyuls-sur-mer, NW Mediterranean. We analyzed different fractions of organic matter (OM) and several biological and chemical water-column variables. We used this dataset to identify the environmental parameters influencing the quality and quantity of dissolved organic matter, and to evaluate the evolution of the different fractions of OM in relation to other biological variables. Finally, we explore the variability of inorganic nutrient and chlorophyll concentrations, at different temporal scales, using a larger data set (since January 2000) from the SOLA station.

2. MATERIAL AND METHODS

2.1. Site and sample collection

Samples were taken from a NW Mediterranean coastal station (SOLA station 42°29'300 N - 03 °08'700 E), located in the Bay of Banyuls-sur-mer (Fig.1). SOLA station was sampled weekly aboard RV "Nereis II" from February 2013 to April 2014. Seawater samples were collected at 3 m depth, and taken directly from Niskin bottles. Vertical profiles of temperature and salinity were simultaneously performed using a CTD (Conductivity-Temperature-Depth, Seabird 19). The data for the 2000-2012 period were acquired from the French Coastline Observation Service (http://somlit.epoc.u-bordeaux1.fr/fr).

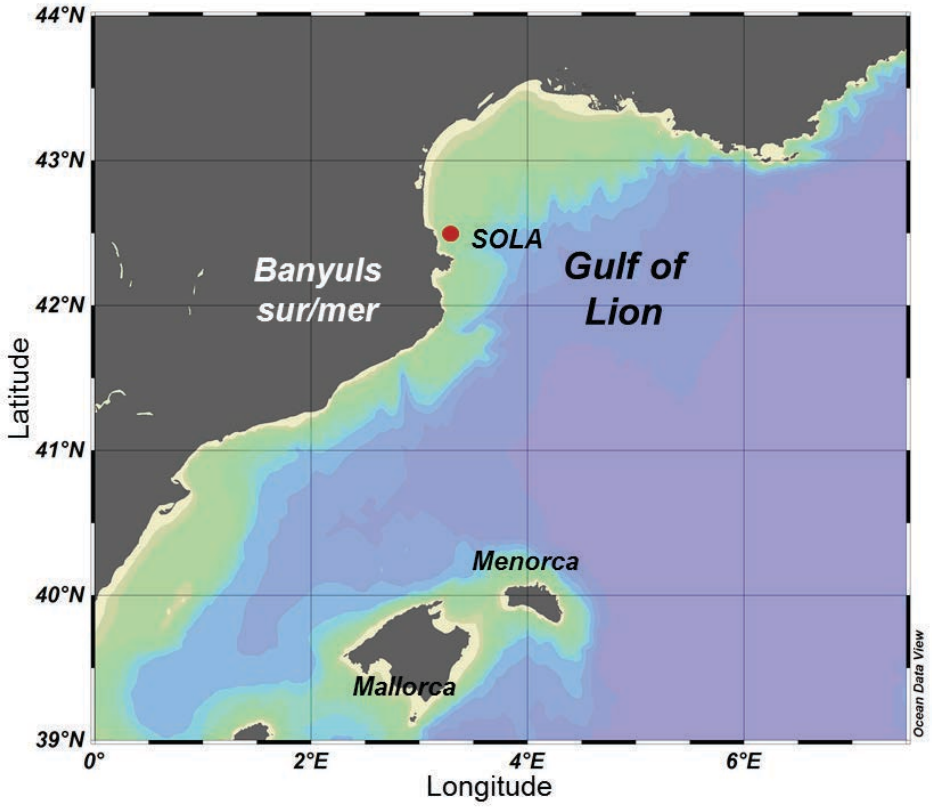

Figure 1. Localization of the study site (SOLA station) in the Bay of Banyuls-sur-mer, NW Mediterranean Sea.

2.2. Chemical and biological analyses

Chlorophyll concentration was determined by fluorometry, filtering 250 ml subsamples on Whatman GF/F filters extracted in 90% acetone and stored at -20^{0}C for 24h in the dark until analysis, using a Tuner Design 10-AU fluorometer (Holm-Hansen et al. 1965). Samples for nutrients analyses (NO^-_3, NH_4^+, PO_4^{-3} and H_4SiO_4) were collected in 12 ml polyethylene tubes, and stored at –20 ^{0}C until analysis in the laboratory using a colorimetric "AA3 AXFLOW/SEAL AAHR" auto-analyzer. Accuracy of measurements was ±0.05 µmol L^{-1} for nitrate (NO^-_3) and silicates (H_4SiO_4), ±0.006 µmol L^{-1} for ammonium (NH_4^+) and ±0.003-0.006 µmol L^{-1} for phosphate (PO_4^{-3}). Ammonium concentrations were obtained using the ophthaldialdehyde method (Holmes et al. 1999).

Samples for analyses of dissolved organic carbon (DOC) were filtered through Whatman GF/F filters and collected in pre-combusted glass ampoules (12 h at 450 ^{0}C). The orthophosphoric acid (H_3PO_4) was added to acidify the DOC samples, and the ampoules were heat sealed and stored in the dark until analysis. DOC was analysed following the high temperature catalytic oxidation (HTCO) technique (Sugimura and Suzuki, 1998, Cauwet, 1994, 1999) using a Shimadzu TOC-L analyser. The system was calibrated daily with a solution of acetanilide (C_8H_9NO MW= 135.17). The DOC concentration was determined by subtracting the blank samples.

Samples for analyses of particulate organic carbon (POC) were filtered on pre-combusted (24 h, 450°C) glass fiber filters (Whatman GF/F, 25 mm). Filters were dried overnight at 50°C, and stored in ashed glass vial in a desiccator, after they analyzed according to the wet oxidation method described by Pujo-Pay & Raimbault (1994) using a CHN Perking Elmer 2400.

Abundance of prokaryotic cells was counted with a FACScan by flow cytometry equipped with argon-ion laser (488 nm excitation) and three fluorescence sensors (FL1: 530/30 nm; FL2: 575/26 nm and FL3: 650 LP). For each sample, 1.5 ml of water was collected and fixed with 25% glutaraldehyde (final concentration 1%), left at room temperature in the dark for 15 min to ensure optimal fixation of the cells, and stored at -80 ^{0}C until analysis.

2.3. Optical measurements of CDOM

Samples water for absorption and fluorescence of CDOM were taken directly from the Niskin bottle in glass flasks of 250 ml, previously washed and pre-combusted (24 h at 450 ^{0}C) to avoid any contamination. The samples were filtered by gravity onto Whatman GF/F filters (porosity 0.7 µm), preserved in the dark and frozen at -20 ^{0}C until analysis (Hancke et al., 2014). FDOM samples were analyzed no later than three months after collection, following the methodology described by Nieto-Cid et al. (2006). CDOM absorption was measured in 10 cm quartz cuvettes using a Varian Cary UV-VIS spectrophotometer equipped with a 10 cm quartz cell. Absorbance was performed between 250 and 750 at a constant room temperature of 20^{0}C. Milli-Q water was used as blank. The residual backscattering (colloidal material, fine size particle fractions present in the sample) was corrected by subtracting the mean absorbance calculated in the spectral range 600-750 nm. The absorption coefficient ($a_{CDOM}(\lambda)$ in m^{-1}), was calculated as:

$$a_{CDOM}(\lambda)=2.303A(\lambda_{250-700})/L$$

Where Abs (λ) is the absorbance at wavelength λ, and l is the optical path length in m and 2.303 is the factor that transforms natural logarithms to decimal logarithms. The spectral slope was calculated over wavelength range ($S_{250-500}$ and $S_{275-295}$) using linear regressions of the natural log-transformed $a_{CDOM}(\lambda)$ according to Nelson et al. (2004) and Helms et al. (2008).

FDOM samples were analyzed with a Perkin Elmer luminescence spectrometer LS 55 equipped with a xenon discharge lamp, equivalent to 20 kW. Slit widths were 10.0 nm for the wavelengths of excitation and emission, and the scan speed was 250 nm/min. Matrices (EEMs) were generated by combining 21 synchronous excitation-emission fluorescence spectra of the sample, obtained for excitation wavelength range of 250-450 nm and an offset between the excitation and emission wavelengths of 50 nm the first scan and 250 nm the last scan, using a Perkin Elmer LS 55 instrument, that was calibrated with quinine sulfate dehydrate

(QS) standard made up in 0.05 mol liter^{-1} of sulfuric acid (Nieto-Cid et al., 2006). Milli-Q water was used as blank and Raman scattering was corrected subtracting the Milli-Q water. We used a combination of different pairs of excitation-emission (EX/EM) wavelengths previously described by Coble (1996) in order to compare our results with previous works. Peak–C (Ex/Em 340-350/420-480 nm) as indicator of terrestrial-like substances; Peak–M (Ex/Em 312-320/380-420 nm) as indicator of marine-like substances and Peak–T (Ex/Em 280/350 nm) as indicator of protein-like substances. Fluorescence measurements were expressed in Quinine Sulfate Units (QSU).

The fluorescence quantum yield at 340 nm was determined using the ratio of the absorption coefficient at 340 nm and the corresponding fluorescence emission between 400 and 600 nm of the water sample and referred to the quinine sulfate standard (*QS*) ratio (Green & Blough, 1994):

$$\Phi(340) = \frac{F(400-600)}{a_{CDOM}(340)} \cdot \frac{a_{CDOM}(340)_{QS}}{F(400-600)_{QS}} \cdot \Phi(340)_{QS}$$

Where $a_{CDOM}(340)_{QS}$ is the absorption coefficient of the *QS* standard at 340 nm (in m^{-1}); *F*(400-600) and *F*(400-600)$_{QS}$ are the average integrated fluorescence spectra between 400 and 600 nm at a fixed excitation wavelength of 340 nm (in *QS* units) obtained for each sample and the *QS* standard (Romera-Castillo et al., 2011) $\Phi(340)_{QS}$ is the dimensionless fluorescence quantum yield of the *QS* standard and equals 0.54 (Melhuish, 1961); and $a_{CDOM}(340)$ is the absorption coefficient of each sample at 340 nm. The specific absorption coefficient $a^*_{CDOM}(254)$ was obtained dividing the value $a_{CDOM}(254)$ by the DOC concentration, and expressed in m^2 g C^{-1}.

3. RESULTS

3.1. Physical drivers and annual variability of the measured Parameters

In Figure 2 we show the monthly average of the different environmental parameters monitored from 2000 to 2012 together with the discrete values obtained during the period detailed in this study (February 2013 to April 2014). Temperature followed a clear annual cycle: minimum values occurred in February (9.4 and 12.7 ºC for 2013 and 2014, respectively) and the maxima (24 ºC) were registered in August (Fig. 2a). Salinity ranged from 34.28 to 38.5 and showed two minima, the first one in early spring (March 2013) and the second one in early winter (January 2014) (Fig. 2b). These minima (34.7 and 34.28, respectively) were exceptionally low with regard to the average for the last 15 years (Fig. 2b), and coincided with FDOM maxima (Fig. 3c).

Inorganic nutrient concentrations were always low in summer and high in winter and spring. Nitrate concentrations ranged from 0.2 µmol L^{-1} to 9.2 µmol L^{-1} (Fig. 2c), with values > 5 µmol L^{-1} in early-mid winter (January, 2013 and March, 2014). Ammonium concentration ranged between 0.01 µmol L^{-1} and 0.64 µmol L^{-1} (Fig. 2d) showing remarkably low values in late spring and autumn 2013 (< 0.1 µmol L^{-1}). Phosphate concentration was low (<0.2 µmol L^{-1}) throughout the time series (Fig. 2e). Silicate presented two maxima in March 2013 and January 2014 (9.9 µmol L^{-1} and 11 µmol L^{-1} respectively) (Fig. 2f) coinciding with the salinity minima and with high nitrate values. The N:P (mol:mol) ratio of inorganic dissolved fraction varied from 1 to 130, with values below 16 typically occurring in the summer. Total chlorophyll (Chl *a*) ranged from 0.05 µg L^{-1} to 4.39 µg L^{-1} (Fig. 3a). During the period studied we found two peaks (February, 2013 and January, 2014) with concentrations of 4 µg L^{-1} and 4.39 µg L^{-1}, respectively. The winter chlorophyll peak in 2013 followed a NH_4^+ maximum, while the 2014 peak came after a salinity minimum. By contrast, during summer and spring, Chl *a* was rather low, reaching values of < 0.6 µg L^{-1}.

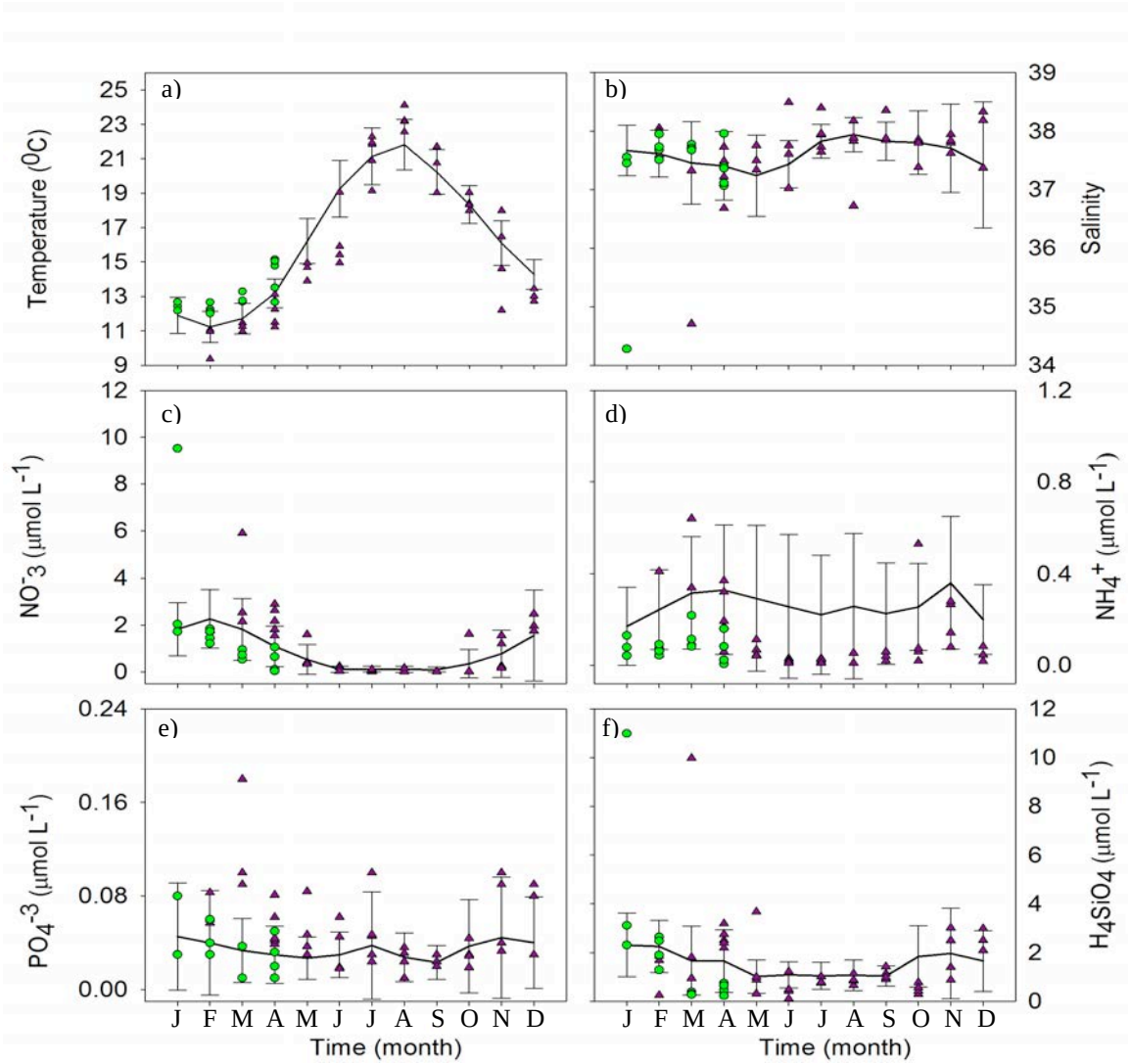

Figure 2. (a) Temperature, (b) salinity, (c) nitrate, (d) ammonium, (e) phosphate and (f) silicate. T is in ^{0}C, and all nutrients are in µmol L^{-1}. Thin lines indicate the average annual cycle of each variable for the 2000-2012 period and vertical bars indicate the standard deviation. Purple triangles and green circles represent 2013 and 2014 sampling, respectively.

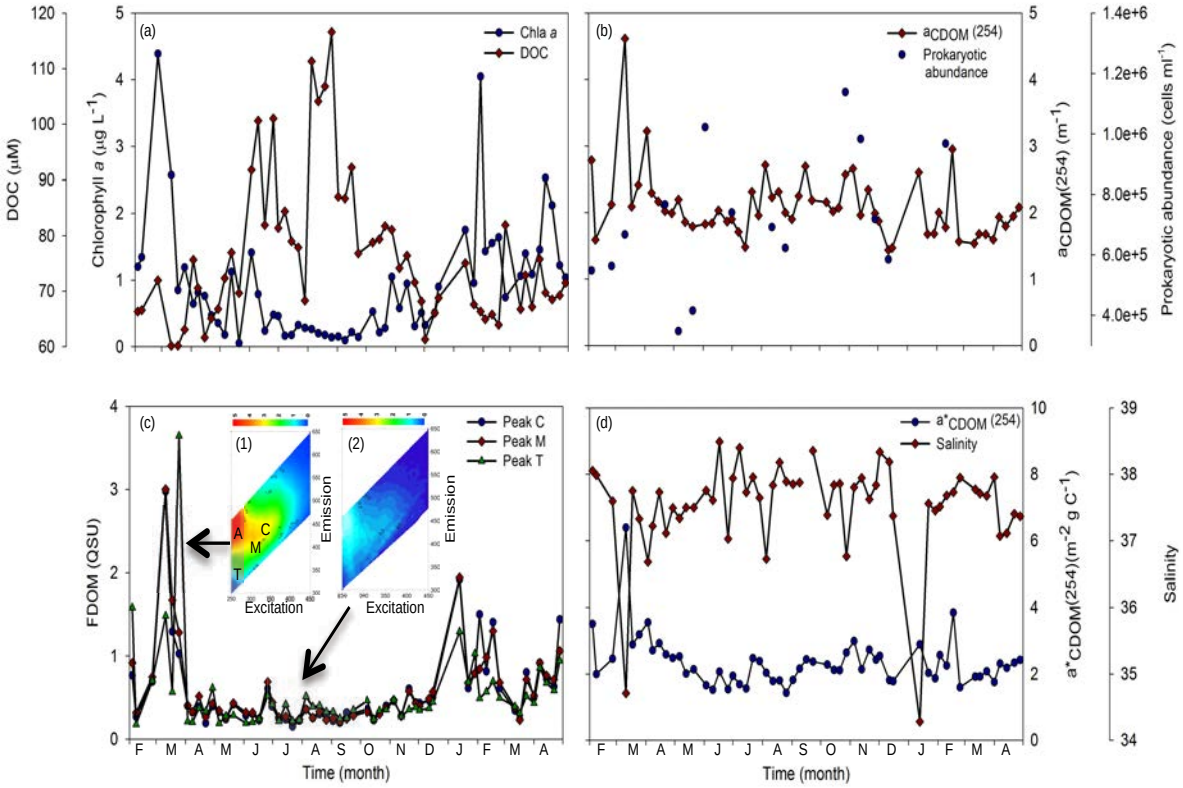

Figure 3. (a) Chlorophyll *a* (chl *a*) in µg L^{-1} and DOC in µmol L^{-1} (b) absorption coefficient at 254 nm [$a_{CDOM}(254)$] in m^{-1} and prokaryotic abundance in cells m^{-1}, (c) fluorescence intensity and excitation-emission matrices (EEMs) in quinine sulfate units (QSU). The EEMs show the two most contrasting environmental events: (1) intrusion of water with low salinity in winter and (2) water photobleached in summer. Inside the EEMs, the capital letters indicate the different peaks, and (d) specific absorption coefficient $a^*_{CDOM}(254)$ in m^2 g C^{-1} and salinity in the Bay of Banyuls-sur-mer (SOLA station) during the time series from February 2013 to April 2014.

DOC concentration ranged between 60 µM and 117 µM. Maximum values occur in mid-summer (August-September), followed by a gradual decrease until the winter period, where DOC values remain low (60.2 to 81.9 µM, Fig. 3a). POC concentrations were high throughout the whole period, except in late summer, when they decreased (~ 58 µM). The highest concentrations of POC occurred in winter and spring 2014 (mean 161 µM). Prokaryotic abundance ranged between $3.48 \cdot 10^5$ cells ml^{-1} to $1.14 \cdot 10^6$ cells ml^{-1} and presented high variability and weak seasonal patterns (Fig. 3b).

3.2. DOM colored fractions

This is the first study for the characterization of optical properties of CDOM within the SOLA time series; therefore comparisons with previous data were not possible. During the first months of sampling EEMs matrices presented marked fluorescence peaks in the areas corresponding to the protein-like and humic-like substances. In the humic-like area, the most intense peaks appeared in March 11, 2013 at 340-350 nm/440-460 nm (peak–C) and at 312-328 nm/420 nm (peak–M) with values of 2.9 and 3.0 QSU respectively. The fluorescence corresponding to protein-like substances (peak–T) ranged from 0.18 to 3.65 QSU and followed temporal trends similar to those of the humic-like substances. EEMs matrices showed a marked seasonal variability with noticeable differences in fluorescence signals associated with the two most contrasting environmental events: (1) the intrusion of water with low salinity in winter and (2) the high light exposure and stratification occurred in summer. During the fresh water inputs, the peaks were clearly defined in the EMM showing high intensities while in summer, a clear decrease in fluorescence intensity was found due to photobleaching (Fig. 3c).

The dynamics of the three peaks is shown in Fig. 3c. The three OM groups follow similar patterns, with high values coinciding with salinity minima and low values along the summer. Accordingly, FDOM-peaks showed significant positive correlation with nutrients (Nitrate and Silicate) and negative correlation with temperature and salinity (Table1).

Table 1. Correlation values between physical and chemical parameters from the sampling period (February 2013 to Avril 2014). Colored cells indicate significant correlation where dark gray = *p*-value ≤ 0.01, light gray= *p*-value ≤ 0.05. T in ^{0}C, nutrients (NO_3^-, PO^{-3}_4, H_4SiO_4, NH^+_4) in µmol L^{-1}, Chl *a* in µg L^{-1}, DOC in µM, Φ340 in %, $a_{CDOM}(254)$ in m^{-1}, Peak-M, Peak-C and Peak-T in quinine sulfate units (QSU) and POC and PON in µg L^{-1}.

	T	S	NO_3^-	PO_4^{-3}	H_4SiO_4	NH_4^+	Chl*a*	DOC	Φ340	$a_{CDOM}(254)$	Peak C	Peak M	Peak T	POC
S	0.21													
NO3	-0.54	-0.75												
PO_4^{-3}	-0.36	-0.39	0.60											
H_4SiO_4	-0.35	-0.74	0.90	0.59										
NH_4^+	-0.37	-0.20	0.31	0.32	0.07									
Chla	-0.56	-0.35	0.36	0.18	0.20	0.21								
DOC	0.74	0.10	-0.41	-0.35	-0.29	-0.30	-0.37							
Φ340	-0.33	-0.25	0.22	-0.04	0.12	0.03	0.39	-0.25						
$a_{CDOM}(254)$	-0.03	-0.58	0.41	0.47	0.48	0.22	0.10	0.00	-0.24					
Peak-C	-0.44	-0.67	0.67	0.47	0.66	0.18	0.51	-0.38	0.43	0.55				
Peak-M	-0.46	-0.68	0.71	0.54	0.67	0.26	0.51	-0.40	0.43	0.55	0.96			
Peak-T	-0.33	-0.35	0.39	0.29	0.27	0.22	0.37	-0.28	0.22	0.32	0.54	0.61		
POC	-0.12	-0.41	0.05	0.05	-0.04	0.03	0.47	-0.11	0.36	0.06	0.30	0.31	0.21	
PON	0.03	-0.31	0.14	0.06	0.17	0.10	0.13	-0.14	0.33	0.18	0.32	0.35	0.08	0.20

The a_{CDOM} at 254 nm ranged between 1.5 and 4.6 ± 0.51 m. The maximum value was observed in mid-winter (11 March 2013), concomitant with low salinity (< 35) and low temperature (12 ^{0}C), but otherwise no clear seasonal patterns were found (Fig. 3b), and did not correlate significantly with temperature (Table 1).

3.3. Optical indexes

None of the calculated a_{CDOM} slopes ($S_{250-500}$, $S_{275-295}$) followed a regular annual pattern. The range and the average of the observed slopes are listed in Table 2. The fluorescence of quantum yield at 340 nm, (Φ340) in SOLA station ranged between 0.08 and 0.87. The highest values of Φ340 (> 0.5%) were observed in winter and spring, however, again, no clear seasonal pattern was detected and a weak correlation with temperature was observed (Table 1). Summer and fall showed a similar Φ340 (mean value 0.29 %). The ratio of $a_{CDOM}(254)$ with respect to the DOC ($a^*_{CDOM}(254)$) was clearly influenced by salinity, the maximum values coincided systematically with the salinity minima (Fig. 3d).

Table 2. Average ± SD of the spectral slopes over the 250-500 nm, 275-295 nm wavelength range, and fluorescence quantum yield at 340 nm (Φ340) from February 2013 to April 2014 in the Bay of Banyuls-sur-mer (SOLA station).

	Average ±SD	Max	Min
$S_{(250-275)}$	0.017 ± 0.005	0.03	0.008
$S_{(275-295)}$	0.029 ± 0.005	0.041	0.016
Φ340	0.30 ± 0.17	0.87	0.08

3.4. Variability trends

The annual range and median values of the different parameters monitored between 2000 and 2014 are shown in Fig. 4. No clear increase of the annual

variability is observed throughout the years. In Figure 5 it is represented the data range, for each season and for the whole study period, of our weekly sampled parameters. The minimum width range of values appeared in the summer for all variables except for DOC and $a_{CDOM}(254)$. Actually, the maximum variability for DOC is observed in summer. In winter we found the maximum fluctuation in chlorophyll values coinciding with those of $a_{CDOM}(254)$ and peak-C.

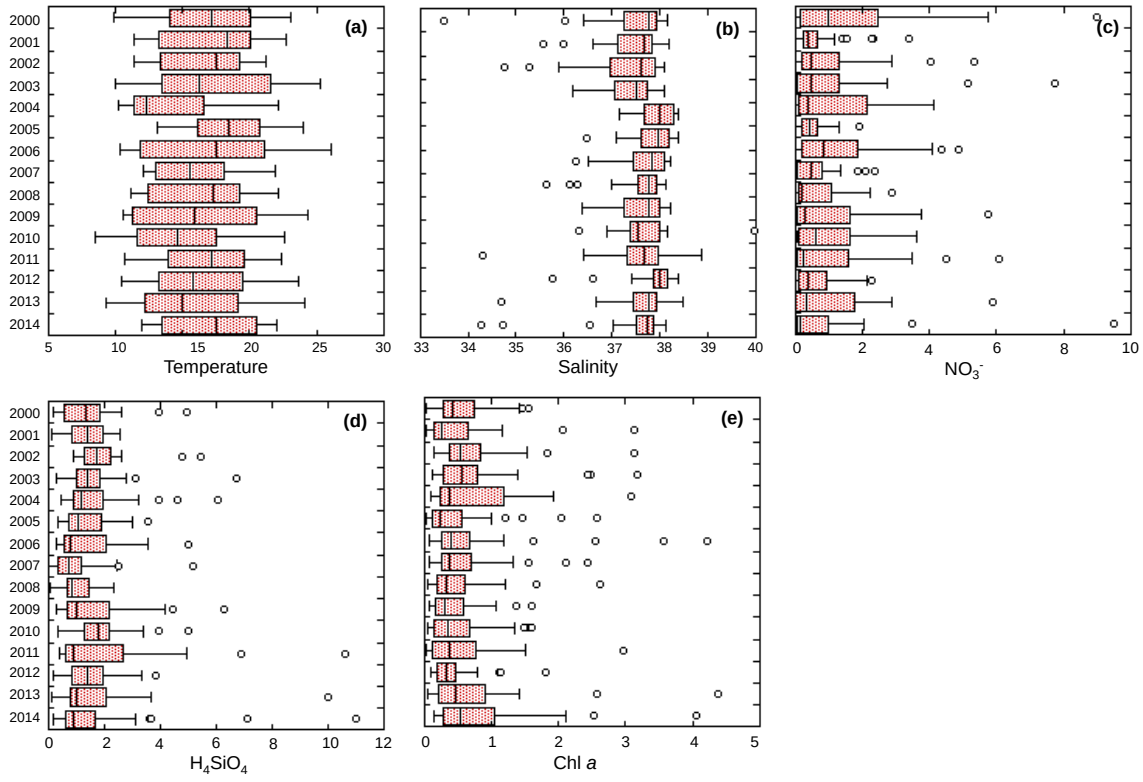

Figure 4. Inter-annual variability of several physical and chemical parameters monitored from 2000 to 2014 in the Bay of Banyuls-sur-mer (SOLA station). (a) Temperature, (b) salinity, (c) nitrate (d) silicates and (e) chlorophyll *a.* The inorganic nutrients are in µmol L^{-1}, temperature is in ^{0}C and chlorophyll *a* (Chl *a*) is in µg L^{-1}. The box encloses 50% of the data; the line inside the box corresponds to the median. The lines extending from the top and the bottom mark the minimum and the maximum values without considering the outliers. The outliers are represented by dots.

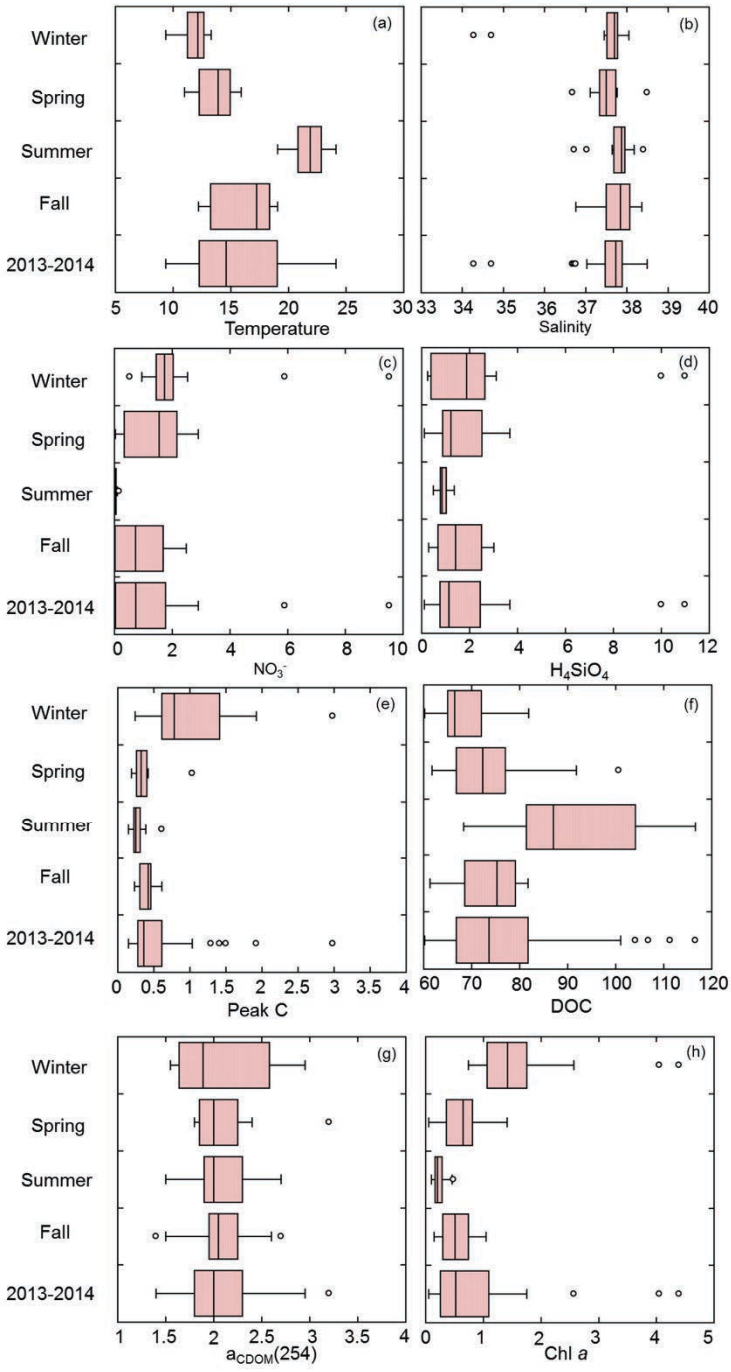

Figure 5. Seasonal versus Inter-annual variability of certain physical and chemical parameters monitored. (a) Temperature, (b) salinity, (c) nitrate, (d) silicates, (e) peak C, (f) dissolved organic matter (DOC), (g) a_{CDOM} (254) and (h) chlorophyll a (Chl *a*) from 2013 to 2014 sampling in the Bay of Banyuls-sur-mer (SOLA station). Temperature in ^{0}C, inorganic nutrients are in µmol L^{-1}, peak C in quinine sulfate units (QSU), DOC in µM, absorption at 254 nm [a_{CDOM} (254)] in m^{-1} and chlorophyll a (Chl a) in µg L^{-1}.

The coefficient of variation (CV) was calculated for each season from 2000 to 2014 in order to explore if, at the seasonal level, we could detect an increase of variability throughout the years (Fig. 6). In general, for all variables examined, low coefficients were found in the summer respect to those found in the rest of the seasons, with the exception of nitrate for which, in general, the lowest CV values were found in winter. In fall, the CVs for temperature and salinity were high at the beginning of the series until 2004, and then relative low values were observed until 2011, thereafter CV increased. No clear temporal pattern was observed for the CV of chlorophyll in any of the seasons.

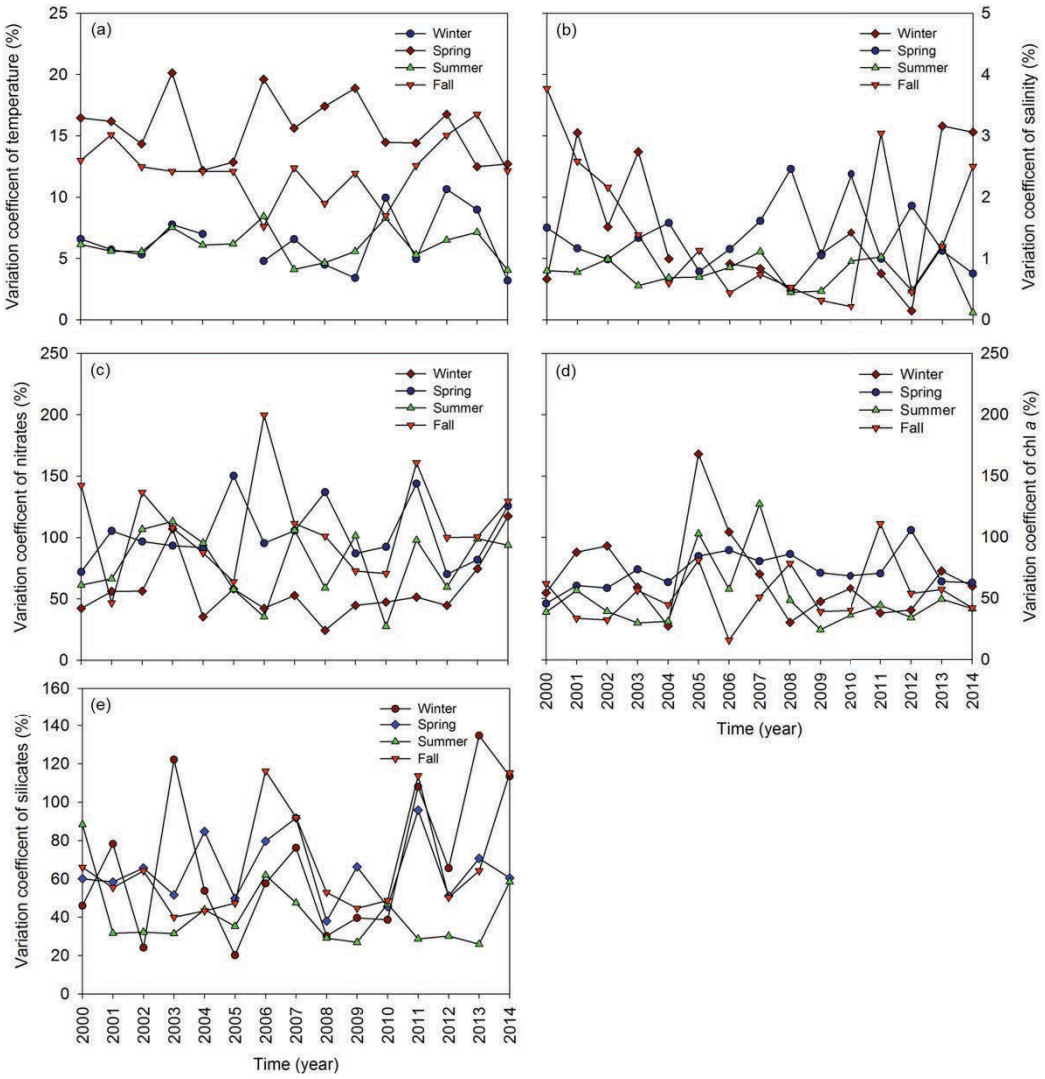

Figure 6. Seasonal coefficient of variation (CV) from 2000 to 2014 in the Bay of Banyuls-sur-mer (SOLA station). (a) Temperature, (b) salinity, (c) nitrates (d) chl *a*, and e) silicates. The CV is expressed in percentage (%).

4. DISCUSSION

4.1. Temporal variability in the Bay of Banyuls-sur-mer

The Bay of Banyuls-sur-mer was characterized by a well-marked seasonal variability, as previously described by other authors (Marty et al., 2002, Estournel et al., 2003, Grémare et al., 2003). The annual changes on temperature and wind intensity drive the formation and the erosion of the thermocline, this together with the seasonal dynamics of river discharges determined the temporal changes of the biogeochemical variables examined. Two sharp decreases of salinity were observed in the winter (March 11, 2013 and January, 13, 2014). Coinciding with the salinity minimum of 2013 we observed high water discharges from the Têt and Tech Rivers (≈ 40 m^3s^{-1} each), and also an exceptionally high level of the Baullaury river (around 200 m^3s^{-1}). Nutrient dynamics was also strongly influenced by these discharges, the nitrate and silicate peaks coincided with the salinity minima and these variables were significantly negative correlated with salinity (R^2 = -0.75, *p-value* < 0.05).

Two maxima of chlorophyll were observed during the study period (25 February 2013 and 29 January 2014). The 2014 maximum occurred after a minimum of salinity; the rapid increase of chlorophyll could be thus the response to the nutrient enrichment produced by freshwater discharge (Fig. 3a). In contrast, the 2013 peak in February 25 occurred just before the salinity drop and coincided with a relative maximum of NH_4^+. This ammonia peak could have been originated from a sediment resuspension process caused by the strong wind observed those days (19 m s^{-1}). High waves and swell have also been reported as a cause for sediment resuspension at the SOLA station (Guizien et al., 2007). In fact, coinciding with this chlorophyll peak we found a relative minimum of temperature. Other authors related these peaks to the development of convective mixing (Béthoux & Prieur, 1983) that typically occurs in winter (Marty et al., 2002). Regardless of the cause of the increase of ammonia, this increase could have induced the phytoplankton bloom in March 2013 where diatoms reached also high abundances (2.0 to 4.0 $\cdot 10^4$ cell L^{-1}, data not shown).

We compare our results with climatological and environmental data collected from 2000 to 2012 in the same station. We found that our results, in general, varied within the range of the values obtained in the past 15 years, there were, however, two

salinity outliers. The annual salinity minima found in our study were also the minima for the last 15 years time series. Considering that these minima are associated to high nutrient concentration, it would be of interest to follow those phenomena in the future to check if they are sporadic events or correspond to a shift in meteorological trends. A proper understanding of such variability will help to better simulate future scenarios and to predict biological production in coastal areas. It is also noticeable that the ammonia concentration showed values always below the mean of the past 15 years, while the phosphate values tended to be above the average. This change of tendency in nutrient dynamics may be due to local processes as it did not occurred in other close areas of the NW Mediterranean (BBMO, http://www.icm.csic.es/bio/projects/icmicrobis/bbmo/).

4.2. Variability at different time scales

Recently it has been reported a high variability and a decrease on seasonality of diverse monitored variables in the coastal regions due to anthropogenic actions and, also, pointed out the difficulty that this brings when looking for responses to human disturbances or to climate change (Cloern & Jassby 2008, Romero et al., 2014). Long and high frequency time series are necessary for a proper understanding of ecosystem processes, yet most of the Mediterranean time series sites are sampled monthly. Here, we used a weekly sampling scheme to examine the temporal variability of several water-column parameters.

We found no evidence of an increase in annual variability since 2000 (Fig. 4), however, looking at the variability corresponding to the summer period (Fig. 6), it is remarkable that along these 15 years the coefficient of variation (CV) of nitrate fluctuated much more than that of the other variables, such as the salinity and the silicate, which usually correlate with nitrate. This mismatch could indicate a possible anthropogenic influence on the nitrate dynamics, as has been suggested by other authors (Iversen et al. 1998; Bouwman et al., 2005; Velasco et al., 2006; Rivett et al. 2008; Taylor & Townsend 2010; Romero et al., 2013, 2014). In fact, the departmental tourism committee has reported that the tourist frequency in the Bay of Banyuls- sur-mer, was about 4.2 times higher in summer than in any other season of the year. This

increase of tourism during summer has been observed since 1997 (http://observatoirecdt66.typepad.fr/frequentation/frquentation_global/index.html). Interestingly the CV of chlorophyll fluctuated less than the CV of nitrates. Unfortunately, we have no data of bacterial production. Also, samples for bacterial abundance were not always taken.

4.3. Temporal mismatch between chlorophyll and organic matter

In order to evaluate the importance of phototrophic components in relation to the total biomass we calculate the proportion of particulate organic carbon respect to the chlorophyll concentration (POC/Chla), which can be considered a proxy for estimating the degree of heterotrophy in a system, at least for a comparative usage in the time series. In Figure 7 we plotted the POC/Chla ratio together with the ratio of total inorganic nitrogen respect to phosphate concentration (N:P, mol:mol). A clear seasonality of both variables can be observed with high values of POC/Chla in summer. The quotients DOC/Chla and (POC+DOC)/Chla exhibited the same pattern (data not shown). Altogether indicating a higher degree of heterotrophy in summer as has been found in other Mediterranean stations (e.g. Alonso-Sáez et al., 2008). These maxima in summer coincide with the minima of N:P values. The higher proportion of particulate organic carbon in relation to chlorophyll in summer could be due, in part, to the use of non-limiting substrates by the osmotrophs to increase in cell size, this mechanism has been proposed by several authors, e.g. Malits et al. (2004) for bacteria and Thingstad et al. (2005) for osmotrophs in general.

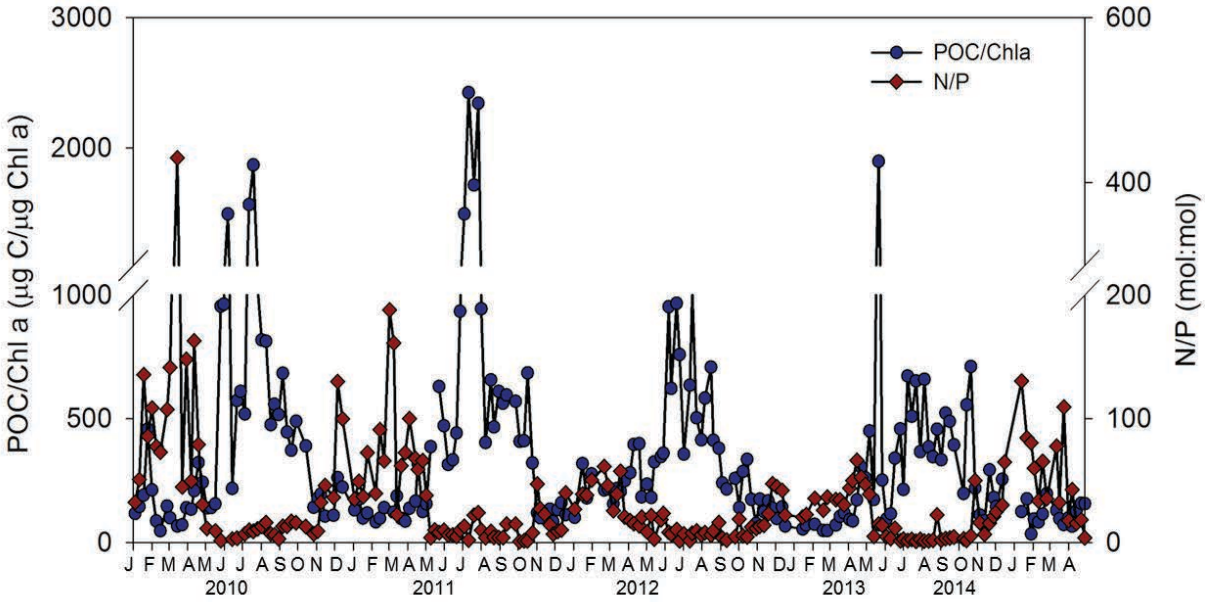

Figure 7. Annual variability of POC/Chla and N/P ratios. The data were available from 2010 to 2014.

The accumulation of DOC in summer in the Mediterranean waters have been attributed to the "malfunction of microbial loop" (Thingstad et al., 1997), these authors, based in some experimental results, associated this mechanism to phosphorous limitation for bacteria, however we found the lowest N/P ratios in summer indicated a nitrogen limitation. In any case, the concentrations of dissolved nitrogen and phosphorous are extremely low in summer (close to detection limits) and probably osmotrophs are limited by both nitrogen and phosphorous. Nevertheless, in other NW Mediterranean sites (Blanes Bay Microbial Observatory, BBMO) it has been found in summer a high bacterial production, measured as leucine incorporation, coinciding with the lowest inorganic nutrient concentrations (Alonso-Sáez et al., 2008). To interpret this mismatch between DOC accumulation and bacterial activity more studies should be done, maybe a top-down control should also be consider. In fact, several studies reported increases of grazing activity with temperature (Marrasé et al., 1992; Vaqué et al., 1994). Unrein et al. (2007) also in BBMO station, found the highest grazing on bacteria rates during the warmer periods.

4.4. Seasonal dynamics of CDOM fractions

The variability of the FDOM peaks in coastal marine systems depends on different physical and biological parameters: the river discharges, the light intensity and the microbial activity, among others. Two fluorescence maxima for humic-like substances were observed in the period studied (March 2013 to January 2014). These peaks coincided with salinity minima and indicate that during the winter the FDOM variability is governed by river discharges, while in spring and summer FDOM dynamics seems to be driven by the light radiation. Low concentrations of humic-like substances were found during the stratification period (April to October) coinciding with high sunlight exposure (in average: day length 14 h/d, irradiance 903 Wm^{-2}). Thus photobleaching could be the major sink process in this period, as the bulk of dissolved organic matter (DOC) was accumulated in this same period. Similar trends have been observed in other coastal areas (Coble, 2007; Para et al., 2010; Romera-Castillo et al., 2013). The DOC maxima in warm periods did not coincide with the FDOM peaks as we could anticipate because the processes that regulate and control these two pools of matter organic are decoupled and are affected by the environment in opposite directions (Chen & Bada 1992; Coble 2007; Romera-Castillo et al., 2013). The statistical analyses confirm this inverse relationship showing a negative correlation between DOC and any of the humic peaks (Table 1).

Regarding the optical indexes examined, the ratio $a_{CDOM}(254)$/DOC showed the highest values coinciding with the two salinity minima, indicating that the intrusion of fresh waters modified not only the quantity but also the quality of the dissolved organic matter. In contrast, the S_{CDOM} values calculated for 250-500 nm did not seem to be influenced by fresh water intrusions as it has been suggested in previous studies (Ferrari, 2000). Also S_{CDOM} shown a clear seasonal pattern and ranged from of 0.011 and 0.023 ± 0.005 m^{-1}, these values are close to those reported by other authors (e.g. Ferrari 2000; Babin et al. 2003; Para et al. 2010; Romera-Castillo et al., 2011). High values of the slope have been also attributed to photobleaching (Vodacek & Blough, 1997). However, other factors should have been influence in our site as we only occasionally found high values of S_{CDOM} during summer (Table 2).

The fluorescence quantum yield at 340 nm, [Φ (340)], again, did not show a clear seasonality, reaching the highest values in winter and spring. This index is

sensitive to both photo and biodegradation (De Haan 1993; Lønborg et al., 2010). Although the values obtained in this study are within the range of others previously reported, the interpretation of Φ (340) variability during our sampling period would require more information about microbial activity.

It is remarkable how DOC seasonal variability changes in relation to other variables. DOC exhibited its highest CV during summer, while most of the other environmental variables studied here got the minimum CV in this warm season. This, again, indicates that for a complete understanding of DOM dynamics more effort should be done during summer not only increasing the sampling frequency but also considering measurements related to prokaryotic activity in the monitoring program (Fig. 5).

4.5. Hypothetical conceptual framework

The flow chart in Figure 8 aims to visualize the major mechanisms that regulate the dynamics of DOM in the temperate oligotrophic (SOLA station). With question marks we indicate the variables for which we do not have data but we do have indirect evidence to hypothesize that these variables or mechanisms play a role in the dynamics of organic matter. This indirect evidence comes from our bulk measurements and/or reported data from similar areas. (Unrein et al., 2007; Alonso-Sáez et al., 2008). The discontinuous line in figure 8 separates the typical recurrent mechanisms occurring in summer season (right side) from those episodic operating at any time over the year, but scarcely during summer. The episodic mechanisms controlling organic matter dynamics are related with abiotic processes (fresh water intrusions, storms, etc.), while DOM in summer is mostly governed by biotic mechanisms (use of non-limiting nutrients, malfunction for microbial-loop and grazing pressure on prokaryotes).

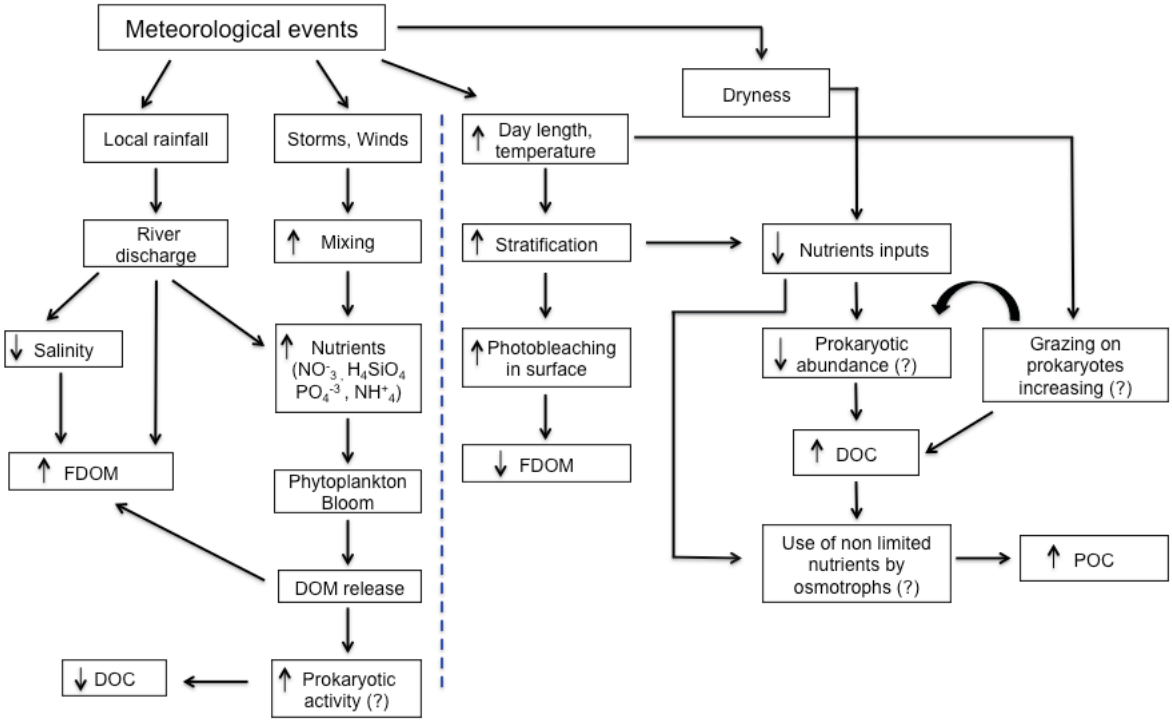

Figure 8. Hypothetical scheme for the ecosystem response to climatology events and photochemical processes in the Bay of Banyuls-sur-mer (SOLA station). The discontinuous line separates the typical recurrent mechanisms occurring in summer season (right side) from those more episodic operating at any time, but scarcely during summer and with question marks we indicate the variables for which we do not have data but we do have indirect evidence to hypothesize that these variables or mechanisms play a role in the dynamics of organic matter.

5. CONCLUSIONS

1. The fluorescent fractions of dissolved organic matter (FDOM) followed opposite trends respect to DOC. This fact is very conspicuous in summer where the minimum values of FDOM are concomitant with the maximum concentrations of DOC.
2. The annual and seasonal variability of environmental variables studied, contrary to what we expected, did not increase along the years.
3. In general, for the variables studied, the variation coefficient in summer was low in relation to the rest of the seasons. The only exception was the case of nitrates for which we found relative high variability in summer. It is suggested that this high variability in summer could be a consequence of anthropogenic activities.
4. We found a mismatch between autotrophic biomass (chlorophyll) and total organic carbon (particulate and dissolved). In summer we observed the highest DOC and POC concentrations concomitant with the lowest chlorophyll values. We postulated that both bottom and top-down mechanisms might operate to explain the organic matter accumulation, among them the “malfunction of microbial-loop”, “the surplus use of non-limiting substrates”, and the predation pressure on osmotrophs.
5. In summer the system dynamics are controlled basically by biological processes, while for the rest of the year the dynamics is clearly marked by episodic meteorological events.

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CHAPTER III

SEASONAL VARIABILITY AND CHARACTERIZATION OF THE DISSOLVED ORGANIC POOL (CDOM/FDOM) AT AN OFFSHORE STATION (NW MEDITERRANEAN SEA)

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ABSTRACT

The offshore station MOLA in the NW Mediterranean is characterized by a convective-mixing throughout winter-spring period followed by a posterior stratification, these two features drive the DOC dynamics in this area. Our objective was to evaluate the effect of the convection event on different environmental parameters, in particular on those related to organic matter in the photic zone. To achieve this objective, we monitored two winter periods corresponding to 2013-2014, which strongly differed in the intensity of the convection processes. Therefore we had the opportunity to compare the system response to contrasting convection-mixing events. Our results showed that the differences in the vertical distribution of biological and chemical variables during the studied period were governed by the marked physical features. The strong convection occurred in 2013 injected nutrients in the euphotic layer favoring a posterior bloom of phytoplankton, but also provoked a dilution of dissolved organic carbon (DOC), colored dissolved organic matter (CDOM) and fluorescent dissolved organic matter (FDOM). In contrast during the weak convection the dissolved organic matter was relatively higher in surface. In the course of stratification period DOC accumulated likely because of the low microbial activity and FDOM decreased probably due to photo-bleaching of the humic-like substances, which causes a diminution in their aromaticity. Our study evidences that in MOLA station, the photo-bleaching is the major sink of FDOM, while the “in situ” production is the main source. Briefly, we could summarize the seasonal variability of FDOM in three episodes (1) A strong convective-mixing in 2013, which dilutes organic matter and injects inorganic nutrients in surface waters favoring a prominent bloom of phytoplankton, (2) a strong stratification, which induces photo-bleaching in summer time and (3) a weak convective-mixing in 2014, which induced lower phytoplankton biomass and an accumulation of DOC.

Key words: CDOM, FDOM, DOC, convective-mixing, stratification, photo-bleaching.

1. INTRODUCTION

A small and variable fraction of dissolved organic matter (DOM) absorbs light in the ultraviolet (UV-R) and visible ranges of light spectrum. This fraction is called chromophoric dissolved organic matter (CDOM) (Hoge et al., 1995). CDOM contributes approximately 20% to the bulk of Dissolved Organic Carbon (DOC) in the open ocean and more than 70% in the coastal environments (Nelson et al., 1998; Siegel, et al., 2002; Kowalczuk et al., 2010). A sub-fraction of this matter can emits blue fluorescence when it is excited by UV-R and is called fluorescent dissolved organic matter (FDOM, Coble, 1996, 2007). The residence time, cycling and fate of CDOM/FDOM in aquatic environments are regulated primarily by biological activity and photoinduced degradation.

CDOM has a significant effect on biological activity in aquatic systems by diminishing light penetration in the water column. Thus, this has a limiting effect on photosynthesis (Arrigo & Brown, 1996), but on the contrary, it protects organisms from DNA damage by harmful UV-R (Williamson et al., 2001; Häder & Sinha, 2005). Absorption of UV-R causes CDOM bleached, reducing its optical density and absorptive capacity. In fact, the CDOM photodegradation can generate compounds of higher biological lability that its precursors, thus favouring microbial activity, and reactive oxygen species, which may damage tissues and alter the bioavailability of limiting trace metals (Mopper & Kieber, 2002). Actually, Organelli et al. (2014) proposes photobleaching as the major cause for CDOM sink in the upper layer.

The characterization of the optical properties of CDOM such as absorption and fluorescence allows the understanding of the DOM dynamics in aquatic environments (Romera-Castillo et al., 2011). Absorption coefficients at different wavelengths and absorption coefficient ratios can also be used as indicators for the molecular size, nature (Carder et al., 1989) and origin (Vodacek & Blough, 1997) of CDOM or as a proxy of photochemical/microbial degradation process (Moran, 2000; Helms et al., 2008). Considering again the optical properties, another indicator, in this case of aromaticity, is the specific absorption coefficient [$a^*_{CDOM}(254)$], also called $SUVA_{254}$ (Helms et al., 2013), which is the ratio of [$a_{CDOM}(254)$] to the DOC (Weishaar et al., 2003). Indeed, the fluorescence can be distinguished into two main groups of

fluorophores, depending on their excitation-emission wavelengths (Coble, 1996). The first group is called humic-like substances, among them the Peak-A emits 250 nm when excited at 350 nm (Coble, 1998) and Peak-M that emits at 320 nm when excited at 410 nm. Both peak A and peak M substances are associated to bio-refractory and photo-labile material (Chen & Bada, 1992). The second group is called protein-like substances, generally associated to Peak-T (280/350), which is considered as a tracer for labile DOM (Yamashita & Tanoue, 2003; Nieto-Cid et al., 2006).

CDOM distribution in coastal environment has been widely studied (Chen & Bada, 1992; Ferrari, 2000; Blough & Del Vecchio, 2002; Romera-Castillo et al., 2013). These authors suggested that the major source of CDOM in these areas is often the fresh water inputs from land, whereas its dynamics depends upon abiotic-biotic interaction processes (Sánchez-Pérez et al. in preparation). Indeed, although variations in CDOM are primarily the result of natural processes, human activities such as: agriculture, effluent discharge, and wetland drainage can affect CDOM varibility. In general, CDOM concentrations are much higher in fresh waters and estuaries than in the open ocean, though concentrations are highly variable and mainly controlled by physical processes such as vertical mixing, ventilation and upwelling of water masses and photochemical bleaching (Helms et al., 2013; Yamashita et al., 2013).

To our knowledge, only few studies have been conducted on CDOM absorption/fluorescence in the Northwestern Mediterranean Sea (Para et al., 2010; Romera-Castillo et al., 2013, Organelli et al., 2014; Xing et al., 2014). In the Gulf of Lion, nutrients and chlorophyll have classic seasonal variations for a temperate zone, with a well-marked surface nutrient enrichment in winter due to vertical mixing, giving rise to a more or less early spring bloom (D'Ortenzio & Ribera d'Alcala, 2009), and then with the apparition of the thermocline and reinforcement of oligotrophic condition during summer (see Mermex Group, 2011 for details).

The aim of the present study is to characterize the vertical distribution and the temporal dynamics of CDOM/FDOM through its concentration and optical properties in a NW Mediterranean oligotrophic site. Also, we endeavor to extract a coherent seasonal signal of the different sources of the DOM components. To achieve these objectives, we monthly sampled in MOLA (Microbial Observatory Laboratory Arago) station between February 2013 and April 2014. This station is a reference site that have been sampled for long time, thus we were able to place our observations in a synoptic biogeochemical context (2007-2014) by the means of the MOLA database.

2. MATERIAL AND METHODS

2.1. Sampling strategy

A monthly sampling of the water column was carried out on board the R/V Nereis II, from February 2013 to April 2014 at the MOLA observation station (Microbial Observatory Laboratory Arago), located in the Gulf of Lion (42°27'21"N – 03°32'57"E; 600 m depth, Fig 1.). Due to particularly severe meteorological conditions during winter, the station could not be sampled from December to February. This station belongs to the MOOSE (Mediterranean Ocean Observing System for the Environment) network (http://www.moose-network.fr/) and is monthly sampled since 2007. Vertical profiles (0-500 m) were performed using a CTD probe from Seabird (Conductivity-Temperature-Depth, SEACAT Profiler CTD SBE 19plus V2). Seawater samples were then collected with 12-L Niskin bottles at six depths in the euphotic layer (5, 20, 40, 80, 120 and 150 m).

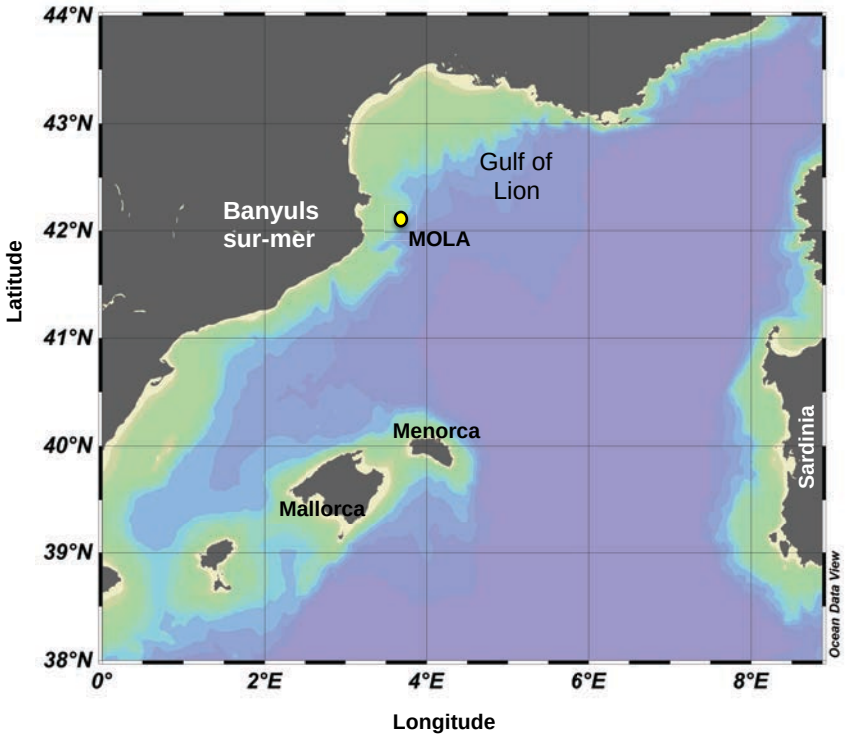

Figure 1. Localization of the study site (MOLA station) in the Bay of Banyuls-sur-mer, NW Mediterranean Sea.

2.2. Physical and chemical parameters

2.2.1. Nutrients analyses

Samples for silicate (H_4SiO_4 ± 0.05 µmol L^{-1}), nitrate (NO^-_3 ± 0.02µmol L^{-1}) and phosphate (PO^{-3}_4 ± 0.01 µmol L^{-1}) were immediately filtered on board (using 0.45 µm cellulose acetate filters) and stored in 20 ml polyethylene vials at -20°C until analysis. In the laboratory, samples were analyzed on a Bran-Luebbe autoanalyzer, according to the colorimetric method modified by Aminot & Kérouel (2007). Ammonium concentrations (NH^+_4 ± 2nM) were determined by nanomolar fluorometric method according to Holmes et al. (1999) on a fluorometer Jasco FP-2020.

2.2.2. Total chlorophyll a

For the samples of chlorophyll, 250 ml of seawater were filtered on Whatman GF/F 25mm glass fiber filters. Filters were stored at -80°C. After extraction by 90% acetone the total chlorophyll (Chla) concentrations were determined by fluorometry on a Turner Design 10-AU fluorometer, according to the method proposed by Strickland & Parson (1997).

2.2.3. Dissolved organic carbon analyses

For dissolved organic carbon (DOC), 20 ml of samples were filtered through 2 precombusted Whatman GF/F filters, then acidified with orthophosphoric acid (H_3PO_4) and stored in pre-combusted glass ampoules (12h at 450°C), in the dark until analysis. DOC concentration was measured by high-temperature catalytic oxidation (Cauwet, 1994) using a Shimadzu TOC-L analyser. The system was calibrated daily with a solution of acetanilide (C_8H_9NO MW= 135.17). The DOC concentration was determined by subtracting the blank samples.

3. Optical properties of CDOM

2.4. Absorption measurements

For the absorption analyses, 250 ml of samples were filtered by gravity through a precombusted GFF filter pre-rinsed with Milli-Q water (Nieto-Cid et al., 2006). Samples were then immediately frozen at -20°C and preserved in the dark until analysis (Hacke et al., 2014).

The absorbance of CDOM was measured throughout the UV and visible spectral domains (250 to 700 nm wavelength) with 1 nm resolution. A baseline with filtered Milli-Q water is used as blank. Spectral absorbance was measured with quartz cuvettes of 10 cm path length using a Varian Cary UV-VIS spectrophotometer. The absorption coefficient was converted using following relationship:

$$a_{CDOM}(\lambda)=2.303A(\lambda_{250-700})/L$$

Where $A(\lambda_{250-700})$ is the spectrophotometric absorbance at wavelength 250-700 nm, L is the optical path length in meters and 2.303 is the logarithmic factor. The specific absorption coefficient at 254 nm [$a^*_{CDOM}(254)$] was calculated dividing the value $a_{CDOM}(254)$ by the DOC concentration and expressed in m^2 g C^{-1}, and this used as a aromaticity index.

3.2. Fluorescence measurements

Samples were stored for less than 3 months in the dark at -20°C (Hancke et al., 2014). Samples were thawed at ambient temperature in following the protocol proposed by Nieto-Cid et al. (2006) using a LS 55 Perkin Elmer luminescence spectrometer equipped with a xenon discharge lamp equivalent to 20 kW. Slit widths were 10 nm for excitation and emission wavelengths and speed scan was 250 nm/min. We performed single measurements of different excitation-emmision wavelengths such as: Peak-A (Ex/Em 260nm /435 nm), Peak-M (Ex/Em 320 nm /410

nm) both peak considered humic-like substances, and Peak-T (Ex/Em 280 nm/ 350 nm) as a proxy of protein-like substances (Coble, 1996).

The fluorescence quantum yield at 340 nm is defined as the portion of light absorbed at 340 nm that is re-emitted as fluorescence. For all samples in this study, the quantum yield [$\Phi_{(340)}$] was determined using the ratio of the absorption coefficient at 340 nm and the corresponding fluorescence emission at 400 to 600 nm and referring it to the equivalent ratio of the quinine sulfate standard (QS) in 0.1N H_2SO_4 using the equation (Green & Blough, 1994):

$$\Phi(340) = \frac{F(400-600)}{a_{CDOM}(340)} \cdot \frac{a_{CDOM}(340)_{QS}}{F(400-600)_{QS}} \cdot \Phi(340)_{QS}$$

Where $a_{CDOM}(340)_{QS}$ is the absorption coefficient of the *QS* standard at 340 nm (in m^{-1}); *F*(400-600) and $F(400\text{-}600)_{QS}$ are the average integrated fluorescence spectra between 400 and 600 nm at a fixed excitation wavelength of 340 nm (in *QS* units) obtained for each sample and the *QS* standard (Romera-Castillo et al., 2011); $\Phi_{(340)QS}$ is the dimensionless fluorescence quantum yield of the *QS* standard and equals 0.54 (Melhuish 1961); and $a_{CDOM}(340)$ is the absorption coefficient of each sample at 340 nm. In this study, Φ(340) was used as a proxy for photochemical processes, as FDOM is more sensitive to light than CDOM (De Haan, 1993).

4. STATISTIC AND GRAPHIC TOOLS

The Pearson's correlation coefficient was used to estimate statistic relationship between variables. Statistical analyses were performed with IBM statistical software (SPSS). The contours plots were obtained with Ocean Data View 4 (ODV).

5. RESULTS

5.1. Hydrological conditions

The offshore water column of the Northwestern Mediterranean has a well-recognized three layers structure (Send et al., 1999) during most of the year. From surface until 250-300 m depth, Modified Atlantic Water (MAW), strongly affected in the upper 100 m by the annual seasonal cycle, is encountered. Between 300 and 700m, Levantine intermediate Water (LIW) is characterized by relative maxima in salinity and temperature, more or less pronounced according to the prospected area. The colder and less salty deeper layer (from 700m to the bottom) is known as Western Mediterranean Deep Water (WMDW) and is formed in the Gulf of Lion in winter, by intense thermohaline convection and/or by cascading of dense coastal water from the continental shelf (Durrieu de Madron et al., 2005).

The 7-years time-series of biogeochemical observations is illustrated for the 0–150 m layer in Fig. 2 and 3 with a specific focus from February 2013 to April 2014. Seasonal changes in temperature and salinity for the surface layer are clearly marked by a succession of stages. The winter convective-mixing period, from December to May, exhibits very low vertical gradient of temperature (around 13°C) and a relative high salinity (>38.10). By the end of April, or early May, there is a gradual increase of the surface temperature (it can exceed 22°C in August) and a decrease in salinity (37.2 to 38 during the stratification period in the surface layer) (Fig. 2a, b). The strengthening of thermal stratification reach the maximum in September and the erosion of the stratification begins under the influence of northwestern winds. Nevertheless, this pattern shows strong seasonal and annual variability as a result of alterations on physical and meteorological forcings. For example, the end of our study (March-April 2014) was clearly marked by relative low salinity in the 0-150 m respect to the whole period (less than 38, Fig. 2b). In a synoptic context, the variability can also be illustrated by the evolution of the depth of the upper mixed layer (UML) in winter (Houpert et al., 2015). Indeed, the depth of the UML can reach the bottom during strong convection in February and/or March. It was the case in 2009 to 2013, whereas in 2007, 2008 and 2014 the maximum depth of the UML was less than 500 m (data not shown).

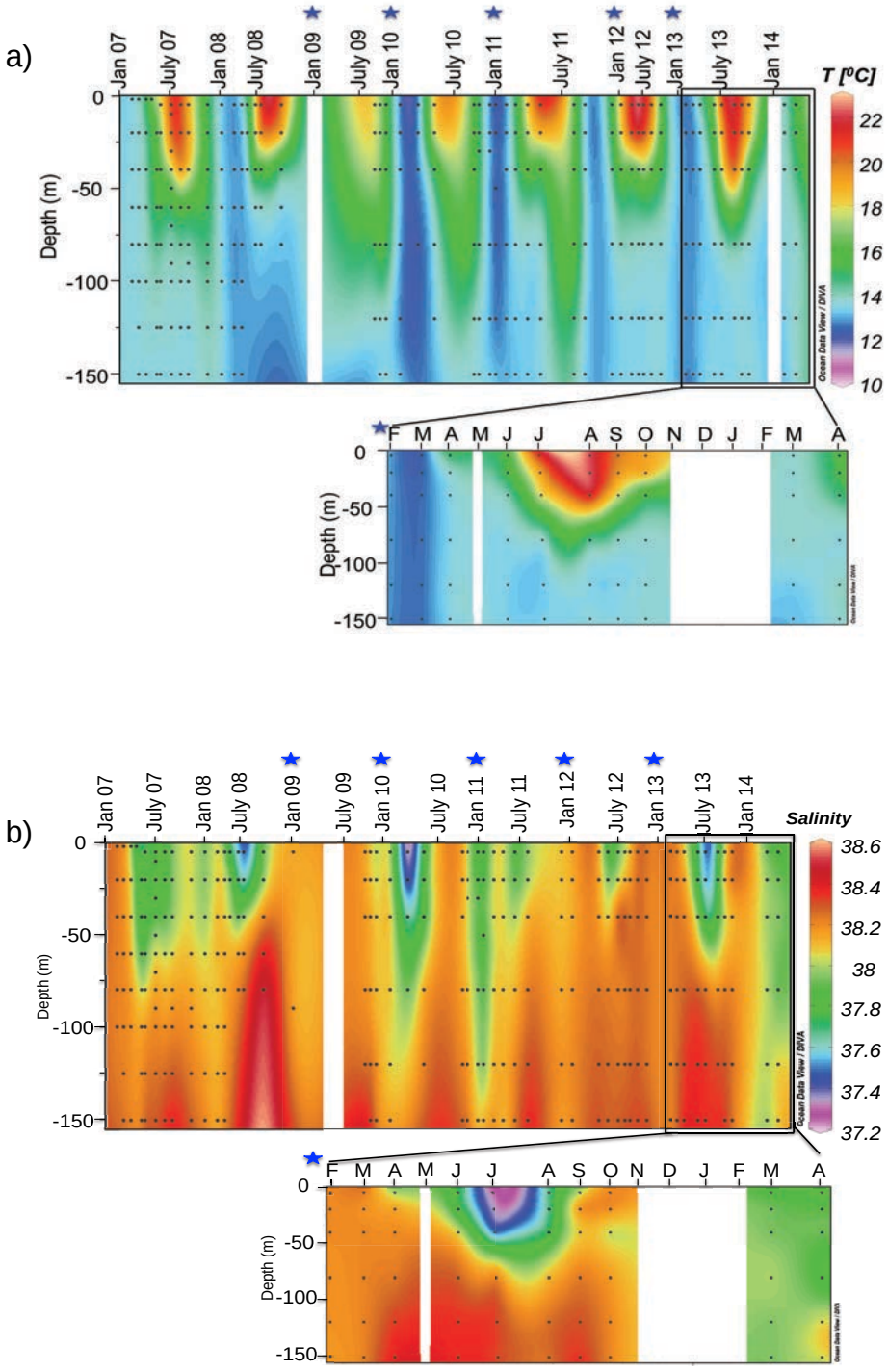

Figure 2. Temporal and spatial variability of a) Temperature and b) Salinity since January 2007 to April 2014. The last year plot is enlarged (the scale of of the colors are shown at the right of the pannel. The dots represent the sampling points and the starts indicate winter strong convection events.

5.2. Nutrients and phytoplankton

Surface nutrient concentrations follow the general pattern of the thermal stratification (Fig. 3). Nitrate (NO^-_3), phosphate (PO^{-3}_4) and silicate (H_4SiO_4) concentrations reach respectively, 1.0-4. µmol L^{-1}, 0.05-0.20 µmol L^{-1} and 1.0-6.0 µmol L^{-1} in the 0-150m surface layers during winter mixing conditions (Fig. 3a, b and c, respectively). In addition, the depth reached by the UML determines the amount of nutrients available in the euphotic layer in spring. This is supported by the weaker nutrient enrichment of the surface layer in 2013-2014 with respective concentrations for NO^-_3, PO^{-3}_4, and H_4SiO_4 less than 2.5, 0.05, and 2.5 µmol L^{-1}, which are half of the concentration measured for the whole period. Concerning the NH^+_4 (Fig. 3d), its concentrations clearly showed a seasonal pattern associated with biological activity.

With the end of winter mixing, nutrient concentrations decrease in the surface layer while increasing stratification from June to November reaching extremely weak levels in surface layer at the end of summer. Then, during summer, a poor nutrient surface layer is separated from a richer deeper layer by well-defined nutriclines (for detailed see Diaz et al., 2000).

Relative homogeneous chlorophyll concentrations are measured in winter 0-150 m layer (between 0.1 and 0.2 µg L^{-1}). The chlorophyll concentrations are maxima in surface layers (0-50 m) during the spring bloom (>1.0 µg L^{-1}) in March and April (Fig. 4). The maximum of chlorophyll biomass becomes less pronounced (0.4 µg L^{-1}) and deepens (around 80 m at the end of summer) following the depth of the nutriclines during summer and fall. In table 1 the correlation between nutrients and other biogeochemical variables are shown. Indeed, Chl *a* concentration had a negative correlation with nutrients ($p < 0.01$). The low nutrients availability in spring 2014 doesn't strongly impact the total Chl *a* concentration. Conversely, the composition of the phytoplankton community shows a high variability. While in March the total number of counted cells does not significantly differ between 2013 and 2014 (~216·103 and 225·103 cells L^{-1}), the abundance of small size cells does differ (Fig.5a). The nanophytoplankton is more abundant in 2014 respect to 2013 (110%), whereas the numbers of diatoms and dinoflagellates are lower in 2014 (25%, 2%,

respectively). In April, by contrast, the abundance of phytoplankton cells, independently of the size class, account for about 30% respect to that of April 2013 ($78 \cdot 10^3$ in 2014, against $243 \cdot 10^3$ cells L^{-1} 2013) (Fig. 5b).

Table 1. Correlation values between physical and chemical parameters from the sampling period (February 2013 to Avril 2014). Colored cells in light gray indicate significant correlation light gray = *p*-value ≤ 0.01. Abreviations: T=temperature (^{0}C), S= salinity nutrients (NO_3^-, PO^{-3}_4, H_4SiO_4, NH^+_4, in µmol L^{-1}), Chl *a*= Chlorophyll (µg L^{-1}), dissolved organic carbon= DOC (µM), quantum yield at 340 nm= Φ340 (%), absorption coefficent at 254 nm = $a_{CDOM}(254)$ (m^{-1}), Humic-like substances = Peak-M and Peak-C, protein-like subtances= Peak-T. All peaks are expressed in quinine sulfate units (QSU), particulate organic carbon and nitrogen= POC and PON (µg L^{-1}).

	T	S	NO^-_3	PO^3_4	NH^+_4	H_4SiO_4	Chl *a*	DOC	Peak-A	Peak-M	Peak-T	ϕ(340)	$a_{CDOM}(340)$
T													
S	-0.64												
NO^-_3	-0.59	0.67											
PO^3_4	-0.43	0.61	0.93										
NH^+_4	-0.07	0.03	-0.14	-0.11									
H_4SiO_4	-0.68	0.81	0.87	0.82	0.01								
Chl *a*	-0.18	-0.23	-0.39	-0.42	0.15	-0.24							
DOC	0.78	-0.57	-0.47	-0.35	0.02	-0.61	-0.22						
Peak-A	-0.12	-0.26	-0.14	-0.22	0.01	-0.13	0.08	-0.09					
Peak-M	-0.23	-0.11	0.10	-0.04	0.02	0.06	-0.02	-0.20	0.90				
Peak-T	-0.12	-0.09	-0.07	-0.16	-0.01	-0.04	0.04	-0.09	0.75	0.70			
ϕ(340)	-0.35	-0.02	0.02	-0.06	0.20	0.08	0.34	-0.24	0.43	0.37	0.32		
$a_{CDOM}(340)$	0.26	0.13	0.11	0.19	-0.15	0.09	-0.42	0.23	-0.28	-0.28	-0.27	-0.72	
$a^*_{CDOM}(254)$	-0.03	0.13	0.10	0.06	-0.19	0.08	-0.13	-0.30	-0.13	-0.09	-0.12	-0.49	0.60

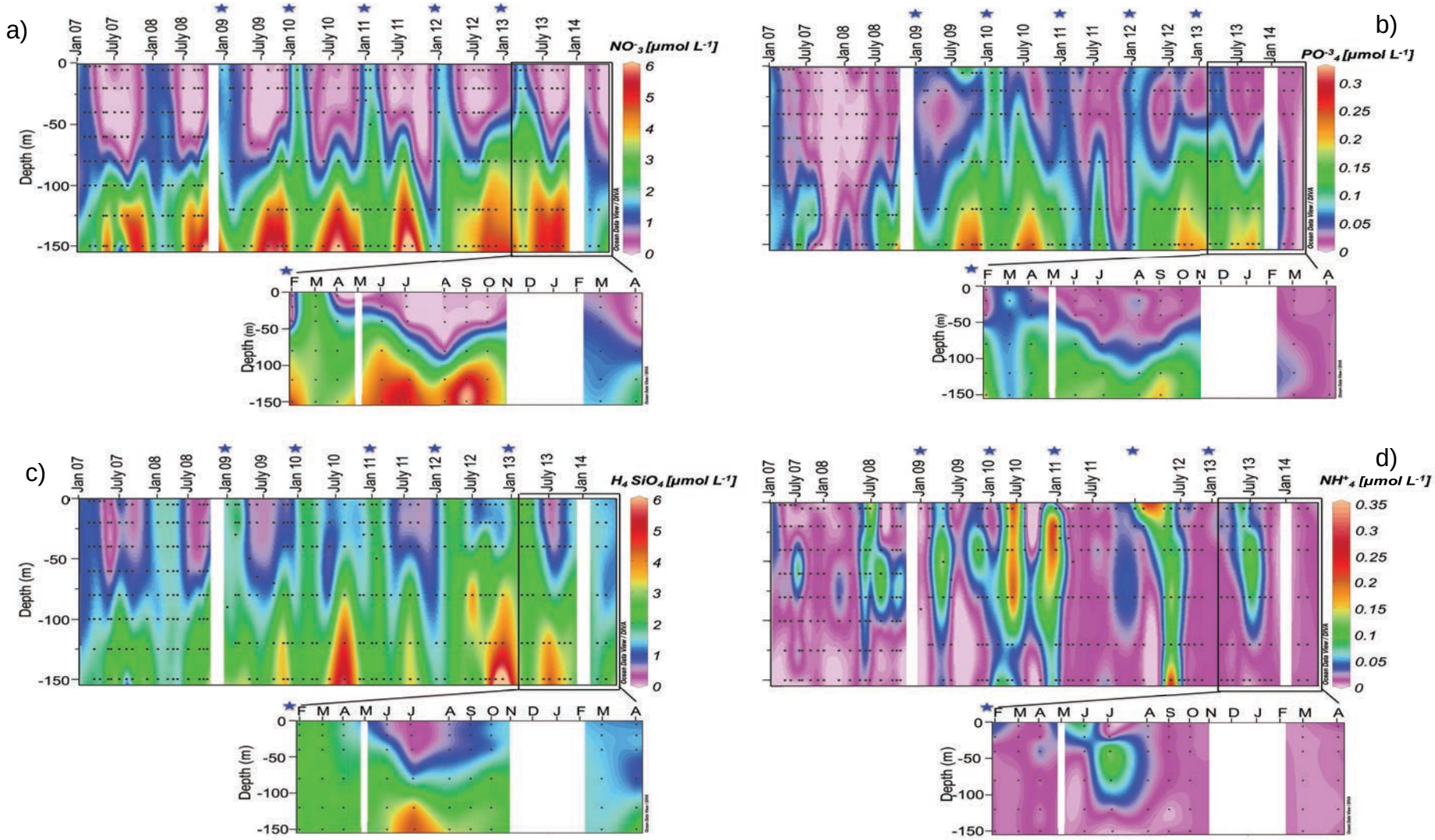

Figure 3. Temporal and spatial variability of a) Nitrates, b) phosphate, c) silicate and d) ammonium since January 2007 to April 2014. The last year plot is enlarged (the scale of of the colors are shown at the right of the pannel. The dots represent the sampling points and the starts indicate winter strong convection events.

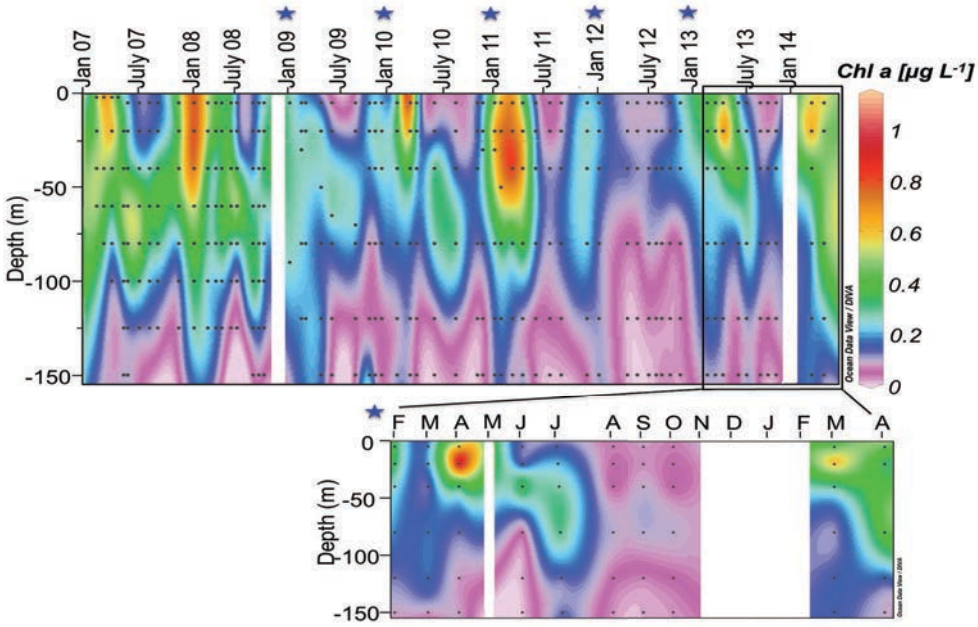

Figure 4. Temporal and spatial variability of chlorophyll *a* since January 2007 to April 2014. The last year plot is enlarged (the scale of of the colors are shown at the right of the pannel. The dots represent the sampling points and the starts indicate winter strong convection events.

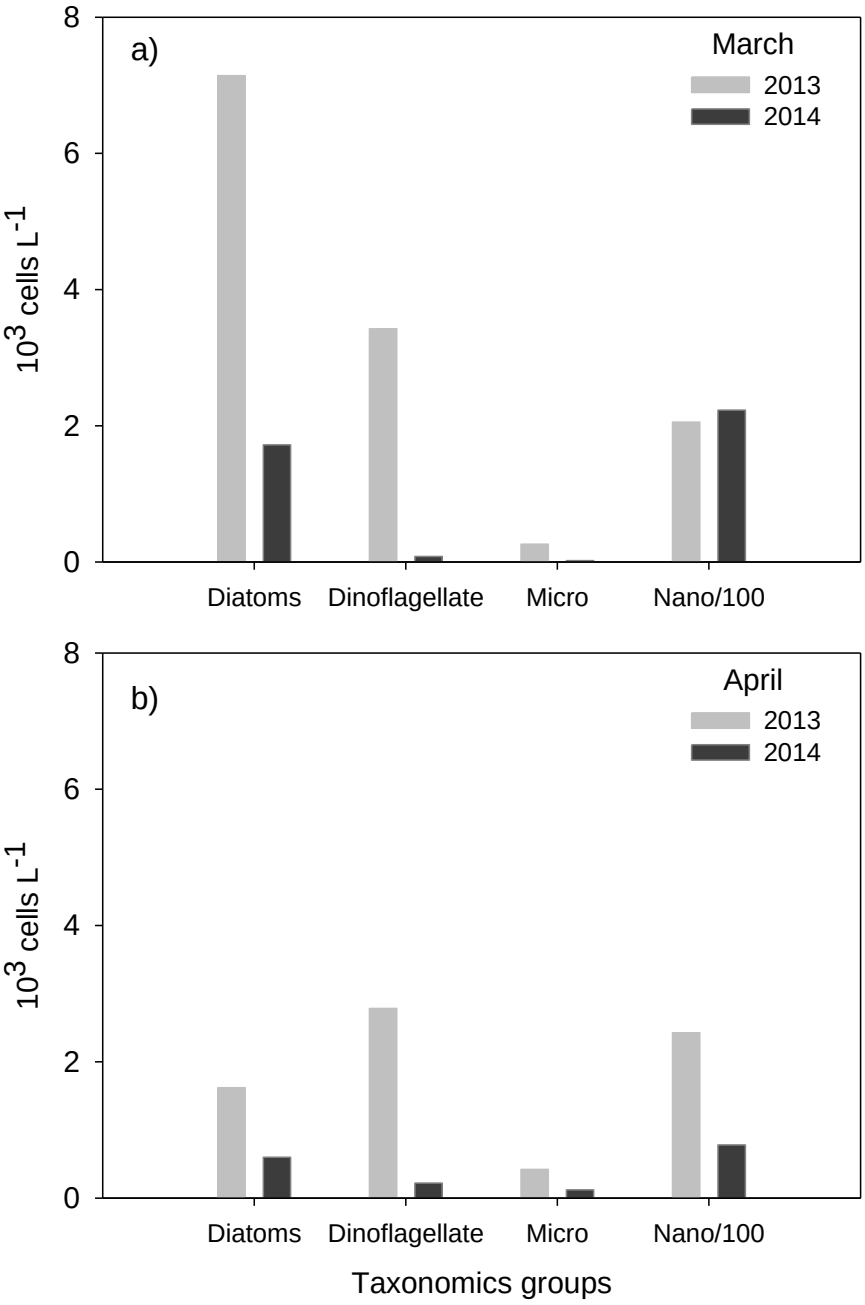

Figure 5. Phytoplankton abundances for March and April (a and b respectively) of 2013 and 2014 at surface (5 m depth) in MOLA station. Note that nanoplankton abundances are divided by 100 to fit in the scale.

5.3. Variability of the DOM stock and composition in 2013 and 2014

5.3.1. Dissolved organic carbon distribution

DOC concentrations showed a well-marked seasonal pattern (Fig. 6) with a clear increase in the upper surface water during the reinforcement of the stratification to reach values close to 100 µM. This accumulated DOC is exported towards deeper layer when stratification broke down during autumn, and DOC concentrations were then uniformly distributed (~50-60 µM in the 0-150 m layer).

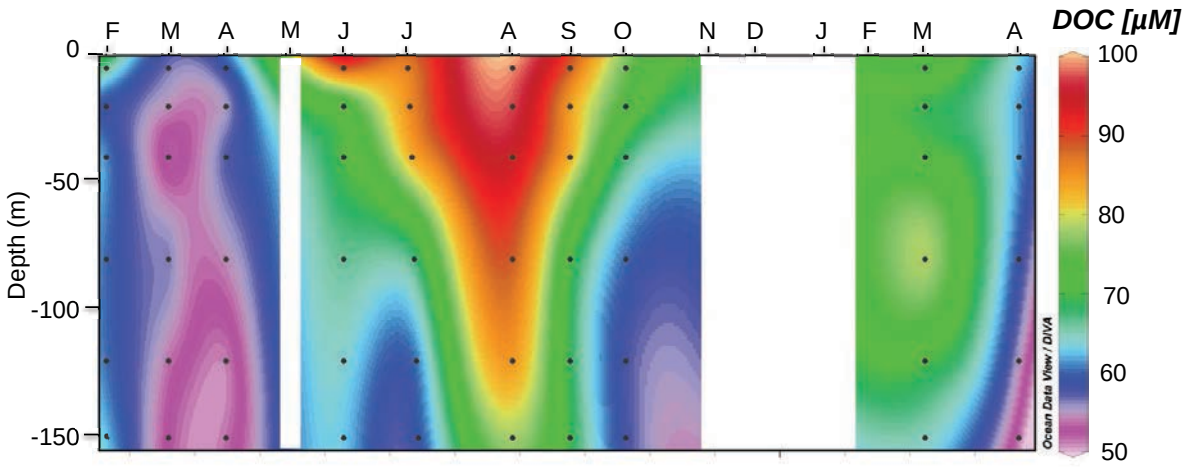

Figure 6. Temporal variability of dissolved organic carbon (DOC). The dots represent the sampling points from February 2013 to April 2014.

5.3.2. FDOM and CDOM variability in 2013 and 2014

Seasonal variability of FDOM peaks showed a similar pattern, minimal values for marine humic-like substances (peak−M) and protein-like substances (peak-T) and slightly higher values showed the peak-A (Fig. 7a, b, c). This values coincide with the stabilization of the water column (May-June) and the minimal $a_{CDOM}(340)$ values. During June-July, the intensity of each peak slightly increases over the whole 0-150 m layer. Peak-A is relatively more pronounced than the 2 others. Then, in August, a maximum appears between 50 and 100 m depth, in association with the DCM. In October and November, vertical mixing progressively homogenizes the water column and high values are measured in the 0-150 m surface layer. In spring 2014 (March-April), we observed a sharp increase in the intensity of the peaks, excepted for peak-M. This variation is associated with the relative low salinity described above.

The $a_{CDOM}(340)$ has relatively low values (≤ 0.8 m^{-1}) over the 0-150m layer during our survey (Fig. 7d). The highest values for a_{CDOM} (340) were found in winter and spring (>0.3 m^{-1} in 0-100 m in February 2013, and also in 0-150 m in February and April 2014). During summer, $a_{CDOM}(340)$ values were low in the euphotic layer (0.05 to 0.25 m^{-1}) but high values could be encountered below (0.40 m^{-1} in June 2013 at 150 m) when minimal values were also encountered around 100 m depth, this pattern was also observed in the quantum yield of fluorescence.

The quantum yield [Φ(340)] of the all samples studied here, ranged between 0.04 and 0.64 %. The highest Φ(340) values were observed in spring. This maximum was consistent with the observed $a^*_{CDOM}(254)$. During the stratification period (June to October) the Φ(340) decrease reaching values between 0.04 and 0.20 % (Fig. 7e).

In general values of the specific absorption coefficient [$a^*_{CDOM}(254)$] oscillated in the ranges between 1.4 and 4 m^2 g C^{-1}. The highest values were found in spring. While $a^*_{CDOM}(254)$ during summer-fall period was low (< 1.2 m^2 g C^{-1}, Fig. 7f).

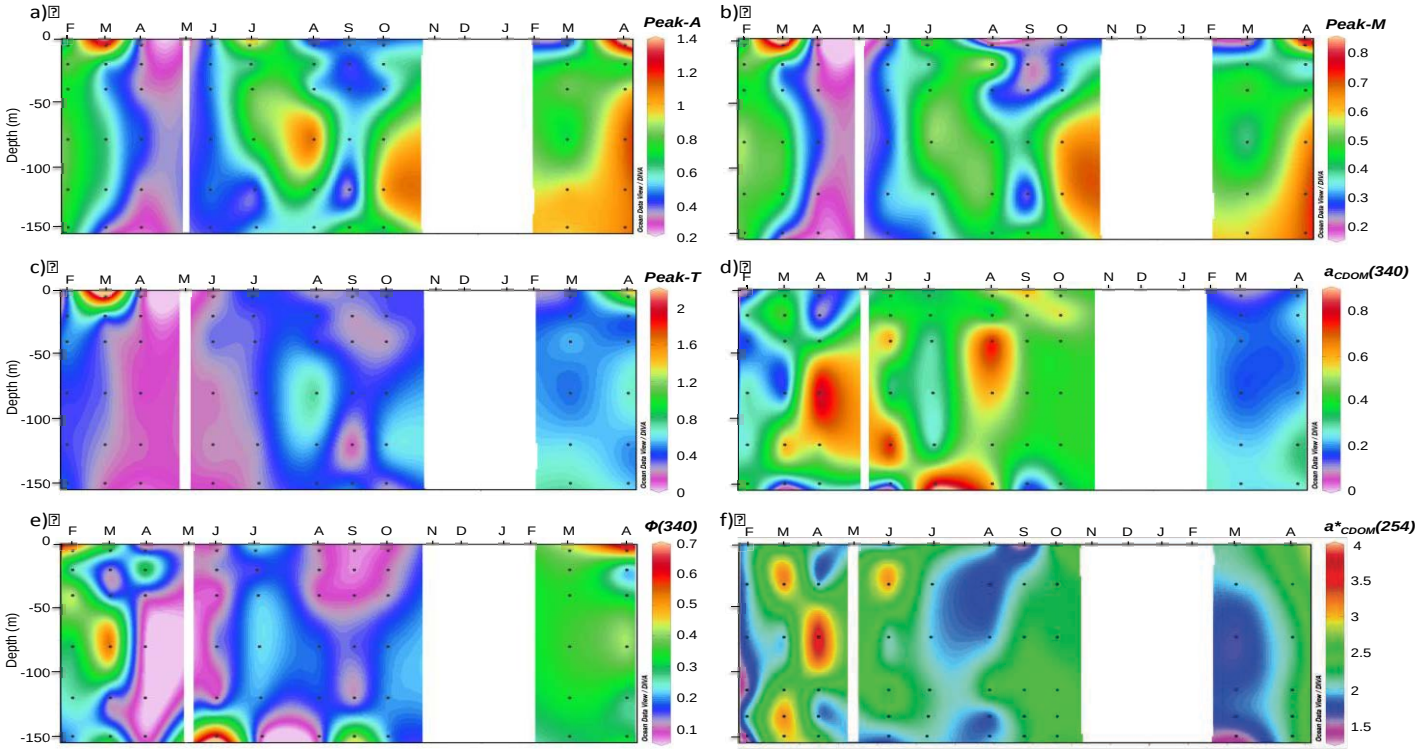

Figure 7. Temporal variability from February 2013 to April 2014. a) Peak-A, b) Peak-M, c) Peak-T. All peaks are expressed in quinine sulfate units (QSU), d) $a_{CDOM}(340)$ in m^{-1}, e) Φ (340) in percentage (%), and f) $a^*_{CDOM}(254)$ in m^2 g C^{-1}. The dots represent the sampling points.

6. DISCUSSION

In our studied area, high values of primary production could be associated with continental rich nutrient outflows, inducing rich zooplankton production in the Gulf of Lion (Diaz et al., 2008) and along the Catalan coast (Garcia & Palomera, 1996). Similarly, high organic carbon input with terrestrial origin stimulates prokaryotic degradation (Sempéré et al., 2000). It is particularly relevant to understand the relation between the source of DOM and its fate, because at various scales, there is a continuous recycling of particulate organic matter (POM) and dissolved organic matter (DOM) to dissolved inorganic matter (DIM) and back again through various microbial processes (Conan et al., 2007; Thingstad et al., 2008). However, the efficiencies of these conversions depend upon not only on quantity but also the quality of DOM. In this sense, new approaches are needed to understand the role of the DOM in the marine ecosystems because the variability of the DOC stock is not representative of its lability. In the Gulf of Lion, the major sources of DOM are river discharges (Para et al., 2010 and references therein) and autochthonous production associated with the recurrent phytoplanktonic bloom (Avril, 2002; Pujo-Pay & Conan, 2003). In late summer, Mediterranean waters are known to be ‘‘greener’’ than expected from their surface Chl *a* concentration because of the presence of Saharan desert dust (Claustre et al., 2002) or due to a higher level of CDOM as well as non-algal detrital particles (Morel et al., 2007). The open Mediterranean Sea allows deep penetration of solar radiation and therefore contains significant photochemical reaction rates. A major sink of DOM is due to sunlight-induced degradation: (1) an abiotic oxidation process involving the direct production of carbon monoxide (CO) and CO_2, and (2) a sequential process of abiotic and biotic reactions involving the photochemical alteration which increases the biological lability of the organic substrates thus facilitating its bacterioplankton utilization (Mopper & Kieber, 2002).

The Mediterranean oligotrophy is essentially induced by the different localizations of the physical and nutrient vertical interfaces (thermocline and nitracline) which are both determined by seasonal temperature changes and by the large-scale circulation (D’Ortenzio & Ribera d’Alcalà, 2009). Though, in the stratified Mediterranean water, the phosphacline is frequently located deeper than the nitracline

and also than the thermocline, inducing abnormally high DIN:DIP ratios in sub-surface waters (Pujo-Pay et al., 2011) at least at the end of summer stratification. This pattern suggests incomplete nitrate utilization by phytoplankton due to the lack of phosphate at the bottom of the photic layer (Diaz et al., 2001). Moreover, the winter deep convection events allow the replenishment of nutrients in the surface layers supporting high phytoplankton productivity (Schroeder et al., 2010). Numerous studies have demonstrated that nutrients availability in the euphotic zone during late winter - early spring is controlled by convective events (Avril, 2002; Goffart et al., 2002; Estournel, 2003; D'Ortenzio, 2012). Thus, a weak winter mixing on the water column could explain the general low nutrients contents on the photic layer during our sampling of spring 2014 (March-April). When convections are intense and deep, the quantity of available nutrients in the photic zone is high, whereas weak winter convection prevents an efficient uplift of nutrients (Marty & Chiaverini, 2010). These authors observed that the frequency of extreme events (high mixing, high nutrients and high biomass) has increased in the recent years, resulting in an increment of phytoplankton biomass in the NW Mediterranean Sea, following a trend that has been observed since 1991 (Marty et al., 2002). These results suggest an augmentation in productivity, contrary to other general models that predict a decrease of primary productivity. From these models, the expected alteration would consist on an enhancement in upper stratification and slower deep-water formation as a response to warming climate (Mermex Group, 2011). However, this warming trend could be partly counterbalanced by a salinity increase due to long-term changes in the freshwater and heat fluxes of the Mediterranean Sea in relation to global change (Béthoux et al., 1999; Millot et al., 2006). Moreover, it has been observed that deep waters of the Western Mediterranean show a rather constant trend towards higher salinity and temperature since the 1980s (Millot, 1987) and this trend significantly affect the biogeochemical properties of the deep-water masses (Schroeder et al., 2010).

6.1. Deep versus weak winter convection. Nutrient and phytoplankton distributions.

During the period studied in detail (February 2013 to April 2014) we found two contrasting situations in terms of intensity of the winter convection; these differences are evidenced by temperature and salinity vertical distributions (Fig. 2a, b). During winter 2013 a deep convection and strong mixing occurred up to 2000 m, bringing nutrients at surface (2 μmol L^{-1} at 5 m, Fig. 3a, c) while in winter 2014 the winter convection observed was rather weak and surface was not enriched as much. Unfortunately we could not sample during the months of January and February of 2014. However, we did have (Fig. 8a, b) and we could also observed the consequences of the convection weakness on terms of nutrients and chlorophyll in the March and April sampling. During this period, moreover, we found low salinity in the first 100 m probably because freshwater discharges. The low salinity values in surface could also favor the stratification of the water column.

When we compare the two winter periods, we found clear differences in the vertical distribution of chemical and biological variables. The high convection in 2013, with high vertical velocity values (Fig. 8b) injected nutrients in surface waters favoring a bloom of phytoplankton with a higher proportion of diatoms than in the 2014, which fits with the conceptual framework proposed in the Margalef's Mandala (Margalef, 1978). In this mandala life-forms of phytoplankton are placed in an ecological space defined by nutrients and turbulence, where the diatoms are associated with rich and turbulent waters, while in the opposite corner of the mandala, small and swimming cells are related to calm and poor waters. Also, in winter 2013 we found more species of larger cell size than in 2014. This could be explained by the higher vertical velocities during winter 2014 and it is in agreement with other studies where it was found a significant correlation between the cell size of phytoplankton and the vertical velocity (Rodriguez et al., 2001). Surprising, in winter 2013 the total number of cells did not reach significant higher values than in 2014, this could be explain a consequence of the differences in the mixing layer depth (MLD). In 2013 the MLD was deeper and the phytoplankton cells could have less light during the day while traveling along the MLD. In any case, in terms of biomass, values were higher in 2013 because we found high abundances of large cell size species, as discussed above.

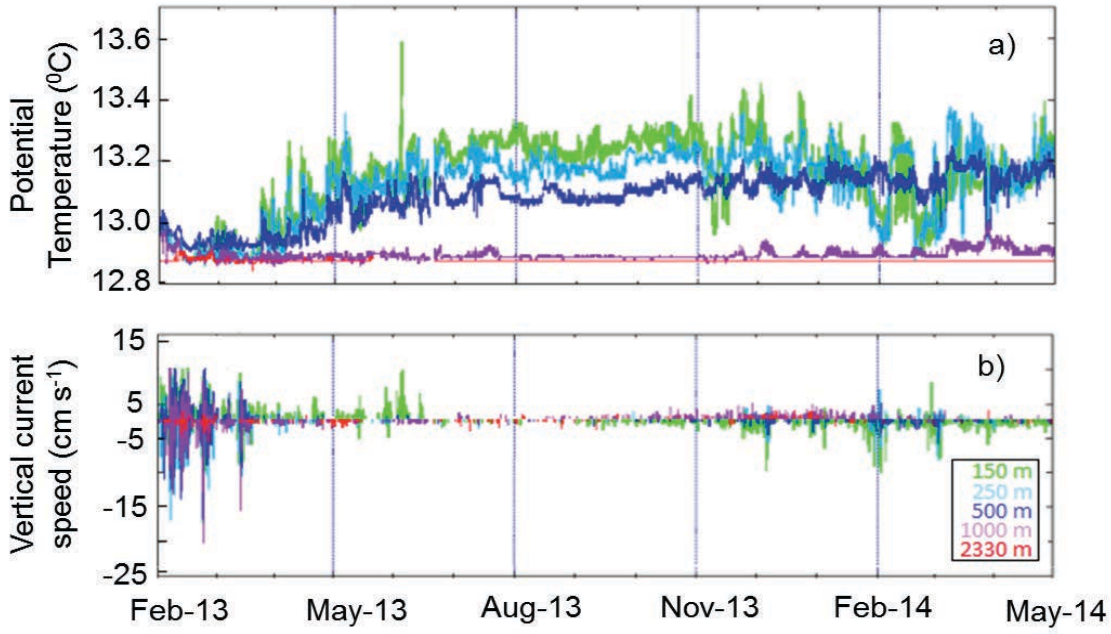

Figure 8. Data of a) potential temperature and b) vertical velocities in the Gulf of Lion from February 2013 to May 2014 until 2330 m depth.

6.2. Seasonal patterns of DOC dynamics

DOC accumulation in the upper layer during summer has been previously described (Avril, 2002; Pujo-Pay et al., 2011). This increase could be related to a low DOC microbial consumption due to the severe limitation for nutrients that bacteria can suffer (Thingstad et al., 1997, Conan et al., 2007) in oligotrophic systems (e.g. NW Mediterranean) during the stratification period (Sambrotto et al., 1993; Kähler & Koeve, 2001).

Thus, DOC accumulates because N- and P-limitation (Sala et al., 2002). We observed a highly significant positive correlation between bulk DOC and temperature ($p < 0.01$, Table 1) indicating a dominant physical control. This is consistent with that reported by Doval & Hansell (2000).

6.3. Distribution of CDOM and FDOM

The vertical mixing, upwelling and convective export together with local biological processes (e.g. phytoplankton exudation and photochemical-bleaching) drive the distribution of CDOM in the open ocean (Nelson & Siegel, 2002). The $a_{CDOM}(340)$ values measured at MOLA during our time series are within the reported values for the open ocean (e.g. Determann et al. 1996; Coble, 2007; Organelli et al. 2014). Discontinuities in CDOM concentration even with relatively high values in the upper layer observed during end of winter to early spring were likely driven by water mixing. At the contrary, the low values of CDOM found during summer-fall period could be attributed to high solar radiation exposure during the stratification period especially in surface layers (Romera-Castillo et al., 2013). Interestingly, the CDOM followed the same trend than chlorophyll does, showing lower concentrations in Spring 2014 in respect to 2013. This coincidence could indicate an in situ production of CDOM by primary producers. The importance of phytoplankton as a source of CDOM has been previously suggested in field studies (Xing et al., 2014) and quantified in the laboratory experiments (Romera-Castillo et al., 2010).

Peaks-A and M followed similar trends over the period studied, with low values along the water column in spring 2013, probably because the dilution caused by the strong convection. Peak-T presented also similar temporal patterns but with very low values perhaps due to the more-labile character of protein-like peak-T in relation to the humic-like peaks. Previous studies in natural water had suggested that protein-like substances (Peak-T) could be released by the phytoplankton (Nieto-Cid et al., 2006). In this case, we observed that phytoplankton biomass peaked also in March (1.74 ng C L^{-1}, unpublished data), suggesting that fluorescence intensity of peak-T could be related to phytoplankton. Briefly, our results showed that changes in the distribution of CDOM and FDOM were closely related to the hydrodynamic conditions and to the chlorophyll dynamics. Therefore, we could summarize the seasonal variability of CDOM and FDOM at MOLA station in three episodes: (1) A strong convective-mixing in 2013, which dilutes organic matter and injects inorganic nutrients in surface waters favoring a prominent bloom of phytoplankton, (2) a strong stratification, which induces photo-bleaching in summertime and (3) a weak convective-mixing in 2014, which induced lower phytoplankton biomass and an accumulation of DOC.

6.4. Optical characterization of CDOM

The fluorescence quantum yield [Φ(340)] for all samples analyzed here were below 1%, which was the mean value obtained in previous studies (Green & Blough, 1994; Vodacek & Blough, 1997; Ferrari, 2000) but yet, similar to those in upper layers of Ría de Vigo (Romera-Castillo et al., 2011) and in NW Mediterranean Sea (Sánchez-Pérez et al., in preparation, see Chapter II). The Φ(340) variations were consistent with the changes observed in $a^*_{CDOM}(254)$. Both indexes are related with the degree of aromaticity of DOM (Benner, 2002). Esteves et al. (2009) suggested that in the open ocean the humic substances have an aliphatic structure and a high content of olefinic compounds, which are the major constituents of humic substances and these should be mainly the result of microbial activity. Weishaar et al. (2003) found that $a^*_{CDOM}(254)$ is strongly correlated with the percentage of aromaticity determined by ^{13}C-nuclear magnetic resonance (^{13}C-NMR) for a large number of humic substances. Therefore the low values of $a^*_{CDOM}(254)$ and Φ(340) could indicate degradation of aromatic compounds and/or highly conjugated DOM fraction and usually they have been attributed to photodegradation from high UV radiation. In fact (Helms et al., 2013) reported that decreases of $a^*_{CDOM}(254)$ is due to the bleaching of specific CDOM fractions of DOM. We found low values of Φ(340) in summer and higher coinciding with the spring bloom. The same pattern was observed for $a^*_{CDOM}(254)$, considering these results, we suggest photobleaching process as a major sink of CDOM in the MOLA station, while the principal source was the "*in situ*" production.

7. CONCLUSIONS

1. The variability of properties of DOM was driven by physical phenomena such as convective-mixing and thermal stratification.

2. Low and vertically uniform FDOM and DOC concentrations was observed during the strong convective-mixing occurred in spring 2013. In contrast, during spring 2014, the weak convective-mixing provoked certain accumulation of DOC and FDOM in surface waters.

3. During the thermal stratification occurring during summer-fall period a decrease in both absorption and fluorescence occurred as a result of photo-bleaching. This photo-bleaching caused a diminution in the aromaticity of humic-like substances.

4. Our results obtained in MOLA station revealed that the photo-bleaching was the major sink of CDOM while the "*in situ"* production as the principal source.

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CHAPTER IV

Dust inputs affect the optical signatures of dissolved organic matter in NW Mediterranean coastal waters

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ABSTRACT

Aeolian inputs of organic and inorganic nutrients to the ocean are important as they can enhance biological production in surface waters, especially in oligotrophic areas like the Mediterranean. The Mediterranean littoral is particularly exposed to both anthropogenic and Saharan aerosol depositions on a more or less regular basis. During the last decades experimental studies have been devoted to examine the effect of inorganic nutrient inputs due to dust on microbial activity. In this study, we performed two experiments in different locations of the NW Mediterranean, where we evaluated the changes in the quality and quantity of dissolved organic matter due to atmospheric inputs of different origin (Saharan and anthropogenic) and its subsequent transformations mediated by microbial activities. In both experiments the humic-like and protein-like substances, and the fluorescence quantum yield increased after addition. In general, these changes in the quality of dissolved organic matter did not significantly affect the prokaryotes. The recalcitrant character of the fluorescent dissolved organic matter (FDOM) associated with dust was confirmed, as we found negligible utilization of chromophoric compounds over the experimental period. We framed these experiments within a two-year time series data set of atmospheric deposition and coastal surface water analyses. These observations showed that both Saharan and anthropogenic aerosols/inputs induced changes in the quality of organic matter, increasing the proportion of FDOM substances. This increase was larger during Saharan dust events than in the absence of Saharan influence.

Keywords: FDOM, dust deposition, DOC, Mediterranean Sea

1. INTRODUCTION

The Mediterranean Sea, due to its low nutrient and chlorophyll concentration is considered as one of the most oligotrophic marine systems (McGill, 1965; Krom et al., 1991; Lucea et al., 2003). During the stratification period, a severe nutrient depletion results in both phytoplankton and bacterioplankton to be strongly limited in phosphorus and/or nitrogen (Béthoux et al., 1998; Thingstad et al., 1998; Sala et al., 2002). However, the climatic conditions and geographic location of the Mediterranean favour the reception of a noticeable dust flux from the Saharan desert (Guieu et al., 2014b). Around of 20 to $50 \cdot 10^6$ tons y^{-1} (Guerzoni et al. 1999) of dust from the Sahara are transported to the Atlantic ocean through the predominant westerly winds and towards the Mediterranean basin influenced by the presence of cyclones (Moulin et al.,1997).

In the Mediterranean Sea, these deposition events occur commonly during spring and summer period (Gallisai et al. 2014). Saharan dust contains soluble nutrients and organic carbon, therefore its deposition in marine waters can favour plankton productivity in the ocean (Prospero et al., 1996; Mahowald et al., 2008). During the last years, the effort to understand the impact of dust deposition on the biogeochemistry of the ocean has increased (Jickells et al., 2005; Suarez et al., 2008). In fact, studies combining field and experimental approaches in several aquatic ecosystems of the Mediterranean region have demonstrated that the Saharan dust stimulated both phytoplankton and bacterioplankton growth (Herut et al., 2005; Eker-Develi et al., 2006; Pulido-Villena et al., 2008; Romero et al., 2011; Guieu et al., 2014a). However, little attention has been paid to the effect of anthropogenic-derived particles, which have a mainly European origin in the NW Mediterranean (e.g. Guerzoni et al., 1999). In addition, in urban coastal places as Barcelona, they also come from local sources. Anthropogenic aerosols in the Barcelona area are also a major source of nitrogen and phosphorous to the atmosphere. Furthermore, they are much richer in organic carbon, particularly in black carbon produced by high temperature combustion processes, than Saharan particles (Querol et al., 2001; Pateraki et al., 2012). On the other hand, anthropogenic aerosols tend to contain high amounts of cupper, lead and other trace metals, which are known to be toxic to microbiota at high concentrations (Jordi et al., 2012; Paytan et al., 2009). Thus one way or another, an effect of anthropogenic aerosols on marine production is also

expected.

Little is known about the impact of aerosols on the fraction of dissolved organic matter that is optically active. This fraction is termed chromophoric dissolved organic matter (CDOM) as it absorbs light. CDOM is a key parameter regulating the penetration of the ultraviolet radiation in the water column and therefore changes in its concentration can alter both primary and secondary production (Smith & Cullen, 1995). A sub-fraction of CDOM that emits light when excited by UV radiation is called fluorescent dissolved organic matter (FDOM). Fluorometric analyses can be used to characterize this sub-fraction. Emission fluorescence spectra can be collected at different excitation wavelengths represented in excitation-emission matrices (EEMs) and different peaks of humic- and protein-like fluorophores can be distinguished (Coble, 1996; 2007). Usually, peak-C and M are associated to humic-like substances, while peak-T corresponds to protein-like substances. The fluorescence intensity of these peaks can be used as indicator of biological (Chen & Bada, 1992) and photochemical processes (Moran, 2000) of the DOM pool.

The optical properties of CDOM are sensitive to biological and physical processes and thus providing valuable information not only of the biogeochemical processes in aquatic environments, but also of the origin of organic matter (OM). In fact, Mladenov et al. (2011) determined that the organic carbon associated with dust inputs can contribute to the dissolved organic matter (DOM) pool in alpine lakes and that the fraction of airborne water-soluble organic matter can contain chromophoric groups similar to humic-like substances. More recently, de Vicente et al. (2012) reported that the chromophoric components related to the dust inputs affected significantly water transparency to ultraviolet radiation.

Our study quantifies the importance of CDOM deposition in the presence and absence of Saharan events and also evaluates the posterior chemical transformations in surface waters by means of CDOM optical signatures. We have collected weekly to biweekly samples of atmospheric deposition during 23 months for FDOM analyses concurrently with surface water samples in the Barcelona coastal area. Within this time frame we have also conducted two aerosols-addition experiments with NW Mediterranean coastal waters, where we have evaluated the prokaryote and FDOM dynamics in response to both Saharan dust and anthropogenic inputs.

2. MATERIALS AND METHODS

5. Time series sampling

We collected samples for atmospheric deposition and seawater analyses over two-year period (September 2012 - July 2014). For atmospheric deposition, one high-density polyethylene (HDPE) container was filled with 500 ml of sterile artificial sterile seawater and left open at the roof of the Institute of Marine Sciences (ICM-CSIC, Barcelona, 41º 23 08'' N, 2º 11' 45.5''E) during one week in summer and two in winter. After this time, subsamples for FDOM were analysed fresh. Seawater samples were taken monthly at 0.5 km offshore of Barcelona (NW Mediterranean, 41º 22' 55'' N, 2º 11' 58'' E). Surface water was collected in 2-L acid cleaned polycarbonate bottles and subsamples for FDOM were analysed freshly.

2.2. Aerosols collection for experiments

The aerosols used in the experiments were collected on Munktell quartz filters (quality 360) using an MCV CAV-A/mb high-volume air sampler. The sampler operated 24 h at 30 m^3 h^{-1}. Filter samples for experimental amendments were obtained at different times in January and March 2014, at the roof of the Institute of Marine Sciences in Barcelona and at the roof of the Center for Advanced Studies of Blanes (CEAB, Blanes, 41° 40' 59.5" N, 2° 48' 2.6" E). Once collected, half of the filters were used for chemical analyses determination and the other half was employed for the amendment experiments. Collected aerosols tend to be a mix from different sources. The classification of aerosols according to the relative percentage of Saharan dust versus anthropogenic origin inputs was done with previous knowledge of the presence of Saharan events based on transport and deposition models and forecasts (www.calima.ws) and on the chemical analyses of the filters. Aerosols of anthropogenic origin tend to have a higher proportion of non-mineral carbon, nitrogen species and phosphorus, while Saharan dust had a higher proportion of silicate and aluminium oxide (Table I).

2.3. Water sampling and experimental design

Our experiments were conducted with water from locations that differed in the degree of oligotrophy. The water was collected at the Blanes Bay Microbial Observatory (41º 40' 0" N, 2º 48' 0" E) on April 8th, 2014 and in the Barcelona coast on May 12th, 2014. Blanes Bay Microbial Observatory is characterized as an oligotrophic area with a chlorophyll annual mean of 0.63 ± 0.05 µg L^{-1} (Guadayol et al.,, 2009). The Barcelona coastal area is less oligotrophic as it receives nutrients from the discharge of two rivers, the Besòs River located in the North of the city and the Llobregat River in the south. The chlorophyll annual average concentration at the Barcelona station is 1.58 ± 1.09 µg L^{-1} (Romero et al., 2014). Both experiments were conducted in mid-spring. This season appears to be the ideal period for testing the impact of dust in surface waters of the Mediterranean Sea, because it is a time interval of the year with frequent dust events (Guerzoni et al., 1997; Gkikas et al., 2009; Gallisai et al., 2014).

. The experiments were termed as BLSp and the second as BCNSp. In both of them the water was collected from the surface layer (approximately 0.5 m depth) and pre-filtered through a 150 µm nylon mesh to remove the larger zooplankton. The water was then transported to the laboratory in 50-L carboys, which had previously been washed with a dilute solution of sodium hypochlorite and exhaustively rinsed with Milli-Q water and were *in situ* rinsed with the sample water itself.

In the laboratory, the water was distributed in 15-L cylindrical methacrylate containers, which were subjected to experimental conditions in a light and temperature controlled chamber during 7 days for the BLSp experiment and during 5 days for BCNSp. Conditions, in duplicate, were: anthropogenic particles enrichment (A), Saharan dust enrichment (S) and control (C) without enrichment. Aerosol concentration added in each container was 0.8 mg L^{-1}. Light conditions were set to 225 µmol photons m^{-2} s^{-1} inside the containers and the light:dark cycle (13 h:11 h) and temperature (17.5 ºC) were adjusted to natural conditions. After placing the containers in the experimental chamber we left them for acclimation before starting the experiment. Because an *in situ* Saharan event occurred the day before BLSp water collection, we increased the acclimation period (up to 45 hours in BLSp with respect to 19 hours in BCNSp) to avoid that the experimental treatment could be

masked by a possible response to the *in situ* input occurred in the field. An initial sample was taken and aerosols were subsequently added as unique dose.

Samples for fluorescence dissolved organic matter (FDOM) and dissolved organic carbon (DOC) were taken on hours 0, 4, 49, 97, and 144 for BLSp experiment and on hours 0, 4, 49 and 97 for BCNSp experiment. Samples for chlorophyll *a* (Chla *a*) and bacteria were taken daily.

2.4. Analytical procedures

2.4.1. CDOM measurements

CDOM absorption was measured in 10 cm quartz cuvettes using a Varian Cary UV-VIS spectrophotometer equipped with a 10 cm quartz cell. Absorbance was performed between 250 and 750 at a constant room temperature of 20 °C. Milli-Q water was used as blank. The residual backscattering (colloidal material, fine size particle fractions present in the sample) was corrected by subtracting the mean absorbance calculated in the spectral range 600-750 nm. The absorption coefficient ($a_{CDOM}(\lambda)$ in m^{-1}), was calculated as:

$$a_{CDOM}(\lambda)=2.303A(\lambda_{250-700})/l$$

Where abs (λ) is the absorbance at wavelength λ, and l is the optical path length in m and 2.303 permits the passage of natural to decadic logarithms.

2.4.2. FDOM measurements

The samples for FDOM were measured immediately after temperature acclimation according to Nieto-Cid et al. (2006). Single measurements and excitation-emission matrices (EEMs) were performed with a Perkin Elmer luminescence spectrometer LS-55 equipped with a xenon discharge lamp, equivalent to 20 kW. Slit widths were set to 10.0 nm for emission and excitation wavelengths; scan speed was

250 nm min^{-1}. Measurements were performed in a 1-cm quartz cell. The EEMs were generated by concatenating 21 synchronous spectra over excitation wavelengths of 250 to 450 nm and emission wavelengths of 300 to 650 nm with an offset between the excitation and emission wavelengths of 50 nm the first scan and 250 nm the last scan. Milli-Q water was used as blank and Raman scattering was corrected by subtracting the Milli-Q water signal. The samples were converted into quinine sulphate units (QSU). The excitation-emission (Ex/Em) wavelengths used for single measurements were described by Coble (1996): Peak-C (Ex/Em 340 nm /440 nm) as indicator of terrestrial-like substances, Peak-M (EX/Em 320 nm /410 nm) as indicator of marine-like substances and Peak-T (Ex/Em 280 nm /420 nm) as indicator of protein-like substances.

Finally, the fluorescence quantum yield at 340 nm, defined as the portion of light absorbed at 340 nm that is re-emitted as fluorescence, [Φ(340)] was determined using the ratio of the absorption coefficient at 340 nm and the corresponding fluorescence emission between 400 and 600 nm of the water sample and referred to the quinine sulphate standard (*QS*) ratio (Green & Blough 1994) :

$$\Phi(340) = \frac{F(400-600)}{a_{CDOM}(340)} \cdot \frac{a_{CDOM}(340)_{QS}}{F(400-600)_{QS}} \cdot \Phi(340)_{QS}$$

Where $a_{CDOM}(340)_{QS}$ is the absorption coefficient of the *QS* standard at 340 nm (in m^{-1}); *F*(400-600) and $F(400\text{-}600)_{QS}$ are the average integrated fluorescence spectra between 400 and 600 nm at a fixed excitation wavelength of 340 nm (in *QS* units) obtained for each sample and the *QS* standard, respectively (Romera-Castillo et al., 2011); $\Phi(340)_{QS}$ is the dimensionless fluorescence quantum yield of the *QS* standard and equals 0.54 (Melhuish, 1961); and $a_{CDOM}(340)$ is the absorption coefficient of each sample at 340 nm. In this study, the ratio, Φ(340), was calculated to add another descriptor of the coloured dissolved organic matter. It has been shown that this ratio increases when microbial transformations dominate with respect to photobleaching and vice versa. (De Hann, 1993; Lønborg et al., 2010).

2.4.3. DOC analysis

Samples for DOC were filtered through Whatman GF/F filters using an acid-cleaned glass filtration system. Approximately 10 mL of water were collected in pre-combusted (450 ºC for 12 h) glass flaks for DOC determination. After acidification with H_3PO_4 (50 µL) to pH < 2 the ampoules were heat-sealed and stored in the dark until analysis. DOC was analysed following the high temperature catalytic oxidation (HTCO) technique (Cauwet, 1994; Sugimura and Suzuki, 1998, Cauwet, 1999) using a Shimadzu TOC-L analyser. The system was calibrated daily with a solution of acetanilide (C_8H_9NO MW= 135.17). The DOC concentration was determined by subtracting the blank samples.

2.4.4. Prokaryotic abundance and chlorophyll *a* determination

Heterotrophic prokaryotic cells were quantified by flow cytometry, according to the method proposed by Gasol & del Giorgio (2000). Samples (1.8 mL) were fixed with 0.18 ml of a 10 % paraformaldehyde and 0.5 % glutaraldehyde mixture. Subsamples of 400 µL were stained with SybrGreen deoxyribonucleic acid fluorochrome and left to stain for 15 min in the dark and then ran at low speed (ca, 30 mL min^{-1}) through a Becton Dickinson FACSCalibur flow cytometer with a laser emitting at 488nm. As standard, 10 µL per sample of a 10^6 mL^{-1} solution of yellow-green 0.92 µm latex beads were added.

For total chlorophyll *a* 30 mL sample was filtered through Whatman GF/F glass fiber filters and subsequently extracted in acetone (90%) and left in the dark at 4ºC for 24 h. The fluorescence of the extract was measured with a Turner Designs fluorometer (Yentsch & Menzel, 1964).

3. RESULTS

3.1. FDOM time series

In order to evaluate the potential role of atmospheric deposition on the dynamics of coastal FDOM, we calculated its proportion respect to the *in situ* seawater concentration during 23 months (September 2012 to July 2014). The results revealed that the deposition of humic-like compounds (peak C and M) and protein-like compounds contributed to an increase of FDOM in surface waters that represents between less than 0.029 and 2% per m^{-3} and per day (Figure 1).

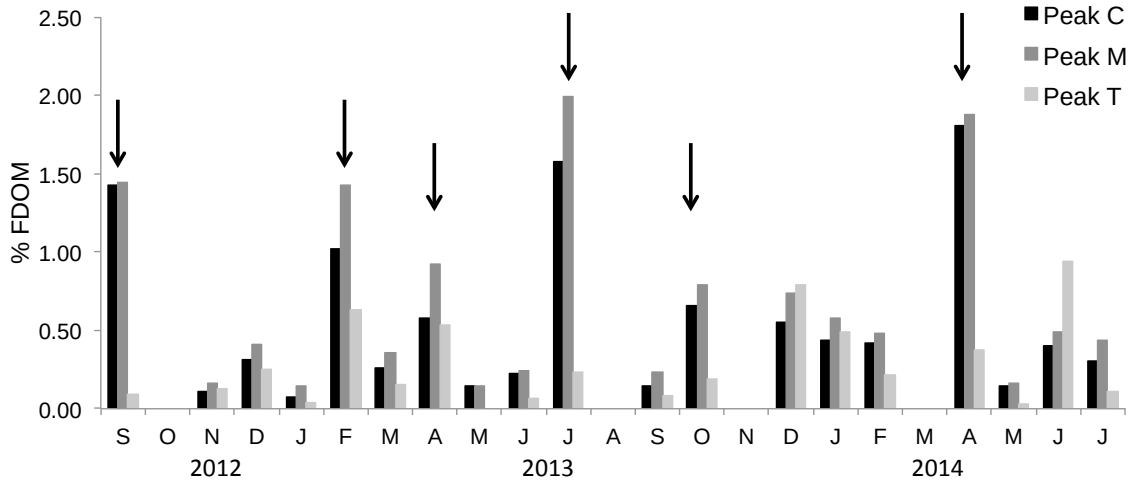

Figure 1. Daily aerosol deposition-derived FDOM flow to the sea surface as a percentage of concentration in Barcelona coastal waters. Humic-like (peak C and peak M) and protein-like (peak T) substances (from September 2012 to July 2014). The arrows indicate the Saharan events.

3.2. Microcosms experiments

3.2.1. Prokaryotic abundance and chlorophyll a

The initial abundance of prokaryotic cells was of $5.04 \cdot 10^5$ cells mL^{-1} in the BLSp experiment and $1.15 \cdot 10^6$ cells mL^{-1} in BCNSp (Fig. 2a, b). In BLSp, we observed a small increase in cell abundance 4 h after the addition in the A treatment and a slightly larger increase in the S treatment. At the end of the incubation (144 h) a larger decrease in abundance was observed in all containers reaching values of $2.6 \cdot 10^5$, $1.06 \cdot 10^5$ and $8.1 \cdot 10^4$ cells mL^{-1} for C, A and S conditions respectively (Fig. 2a). The BCNSp experiment also showed a small increase in prokaryotic abundance following the addition (4 h) in all the treatments. After that, small changes were observed in C treatments, while in S and A conditions the abundance peaked at 28 and 52 hours respectively (Fig. 2b).

Chlorophyll *a*, which is a proxy for phytoplankton biomass, showed in both experiments and in all treatments, no changes immediately after the aerosols addition. However, in BLSp an increase occurred during the course of the incubation, reaching values of 0.51±0.02, 0.74 ±0.02 and 0.56±0.01 µg L^{-1} for C, A and S respectively (Table II). While, in the BCNSp experiment, a peak in S and A containers was observed at day two (Table II) but then a decline of the Chl *a* concentration was observed until the end of the experiment in all containers reaching values of 0.49± 0.05 µg L^{-1} in the last day (Table II).

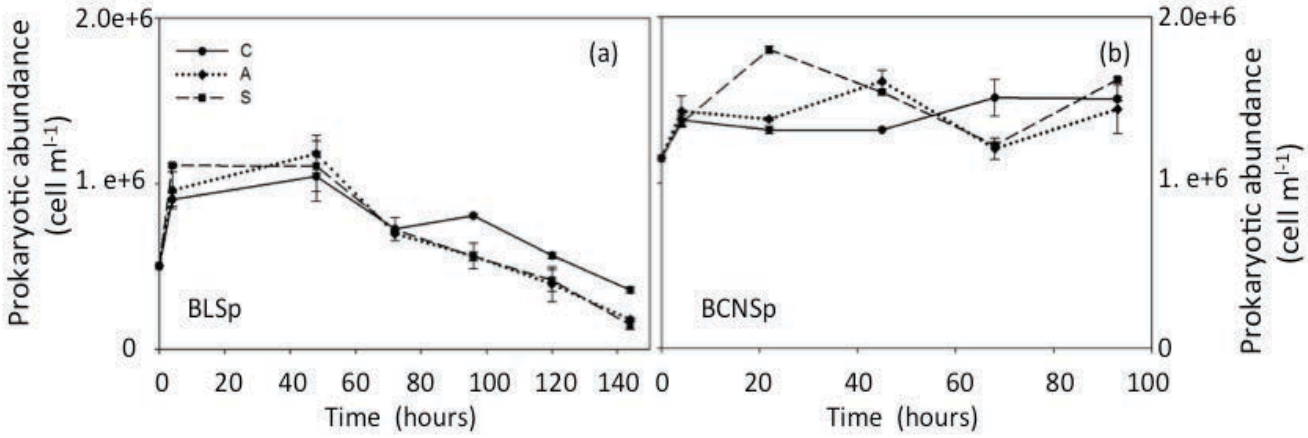

Figure 2. Prokaryotic abundance over time for the three treatments of BLSp (a) and BCNSp (b) experiments. The dust was added at t=4h in both experiments.

3.2.2. DOC and FDOM dynamics

Aerosols did not significantly alter the DOC concentration (Fig. 3d and 4d). The largest difference was found after the anthropogenic addition in the BLSp experiment (Fig. 3d), where it accounted for an increase of about 10% the total DOC concentration. After the enrichment, DOC concentrations were maintained rather constant in all conditions of the BLSp experiment. In the BCNSp experiment, DOC values did not increase immediately after the addition, however an increment at the end of the experiment occurred in all the containers (Fig. 4d).

In both experiments, the increase of humic-like (Fig. 3a, 3b, 4a and 4b) and protein-like (Fig 3c and 4c) substances was higher in the treatment enriched with anthropogenic particles than in the one enriched with Saharan dust. Humic substances reached values about 1.5 QSU in A conditions, while; in treatments C and S the maximum values were about 0.74 and 0.94 QSU respectively. In both BLSp and BCNSp experiments, the different groups of organic matter in all treatments followed similar patterns (Fig. 3a, 3b, 3c, 4a, 4b and 4c). After the initial increase due to dust addition, FDOM values were maintained rather constant during the course of incubation (Fig. 3 and 4).

We compared the FDOM matrices before addition (C) with the changes of FDOM occurred in each experiment after the addition (Fig. 5). In the BLSp experiment, the excitation-emission matrix (EEM) in A treatment presented marked fluorescence peaks in the humic-like and protein-like areas after the addition (reaching concentrations around 1.5 QSU) in comparison to S microcosm, where the increase of fluorescence intensity was minimal (about 0.2-0.3 QSU) and without any defined peak. In the BCNSp experiment, the EEM of the water before the addition (C condition, Fig. 5) showed two peaks at Ex/Em 280 nm/ 350 nm and 250 nm/ 435 nm corresponding to peak-T and peak-A (2.0 and 1.3 QSU respectively). In contrast, the fluorescence in A treatment after the addition presented two peaks within the range of the marine and terrestrial humic-like substances (peak-M and peak-C respectively). These increases were small (about 0.5 to 0.75 QSU) in comparison with BLSp experiment. Finally, the fluorescence alteration after additions in S treatment was low with respect to initial fluorescence intensities (values only increased about 0.1-0.3 QSU in the humic-like area, and about 0.4 QSU in the protein-like area).

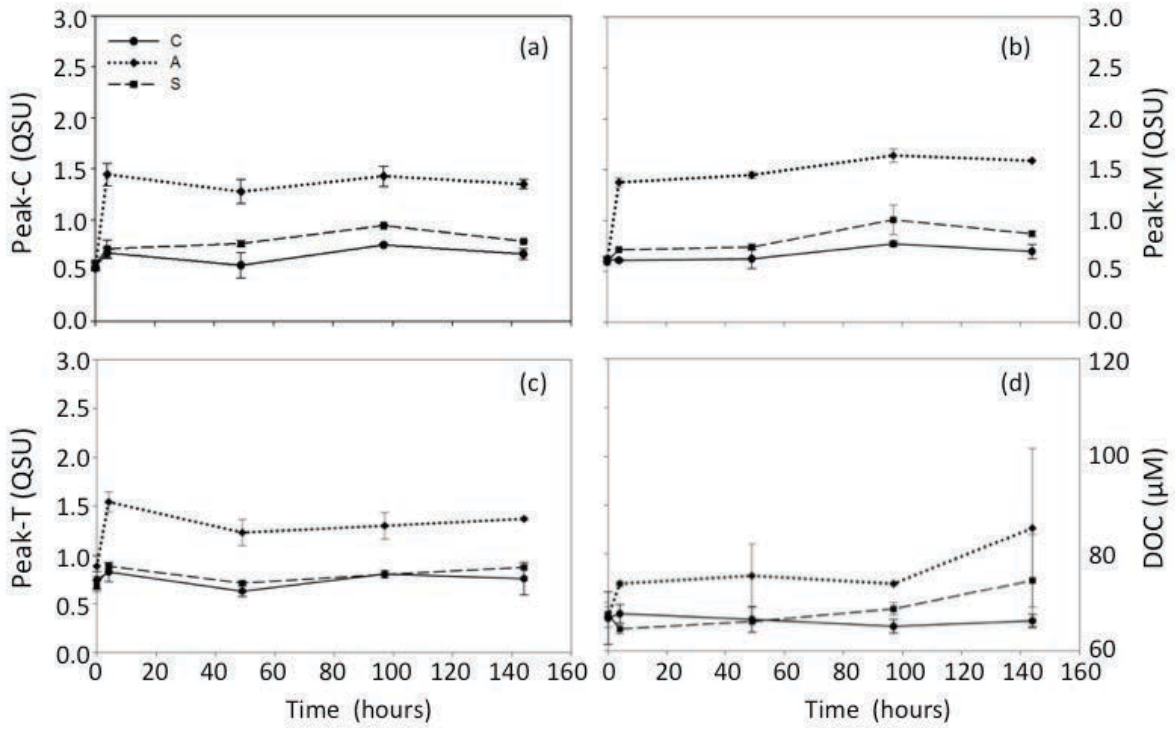

Figure 3. Fluorescence intensities of FDOM peaks during the course of incubation in the BLSp experiment. (a) peak-C, (b) peak-M, (c) peak-T and (d) dissolved organic carbon (DOC). The FDOM peaks are in quinine sulfate units (QSU) and DOC is in µM. The bars indicate the standard deviation.

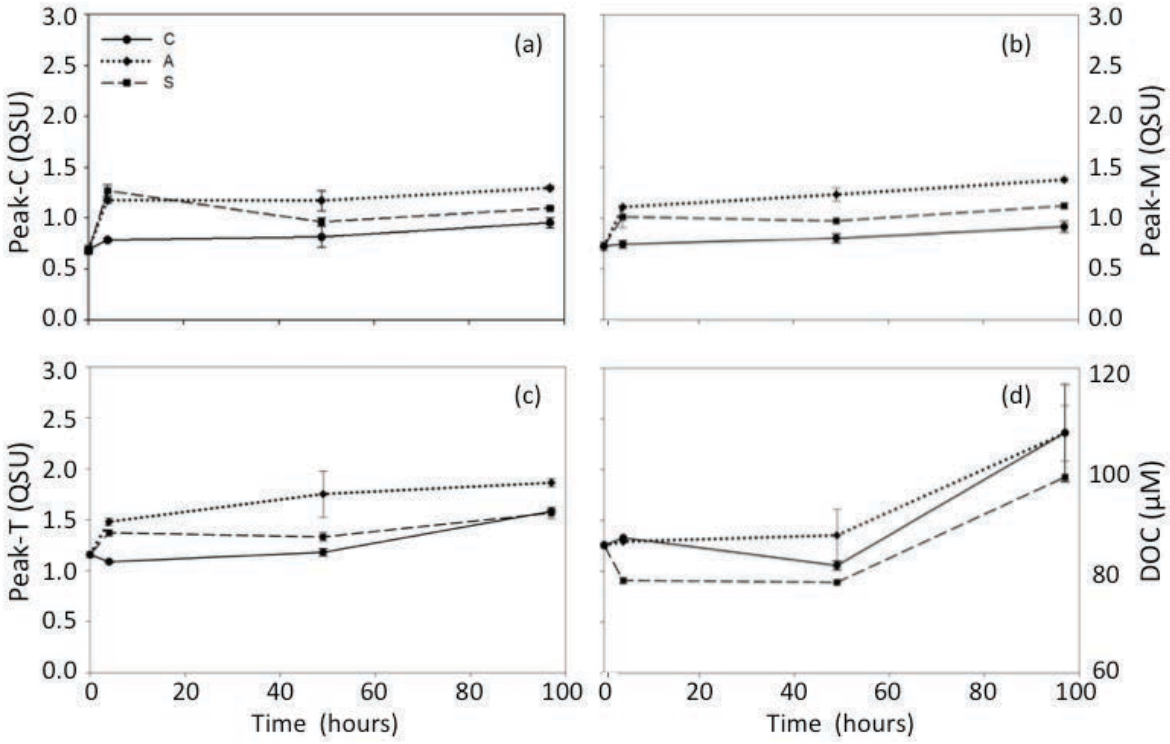

Figure 4. Fluorescence intensities of FDOM peaks during the course of incubation in the BCNSp experiment. (a) peak-C, (b) peak-M, (c) peak-T and (d) dissolved organic carbon (DOC). The FDOM peaks are in quinine sulfate units (QSU) and DOC is in µM. The bars indicate the standard deviation.

Table I. Relative percentage of the composition of the different aerosols used in BLSp and BCNSp experiments respectively. Abbreviations: A= anthropogenic, S=Sahara, OC= organic carbon, CO_3= carbon trioxide, SiO_2= silicate oxide, Al_2O_3= aluminum oxide, NO_3^-= Nitrate, NH_4^+= ammonium and P= phosphorus.

	Blanes (BLSp)		Barcelona (BCNSp)	
	A	S	A	S
OC	31.95%	4.93%	26.38%	6.75%
SiO_2	4.75%	40.64%	13.56%	27.88%
Al_2O_3	1.58%	13.55%	4.51%	9.29%
NO_3^-	11.01%	2.48%	7.81%	2.11%
NH_4^+	2.12%	0.37%	1.47%	0.52%
P	0.10%	0.08%	0.13%	0.07%

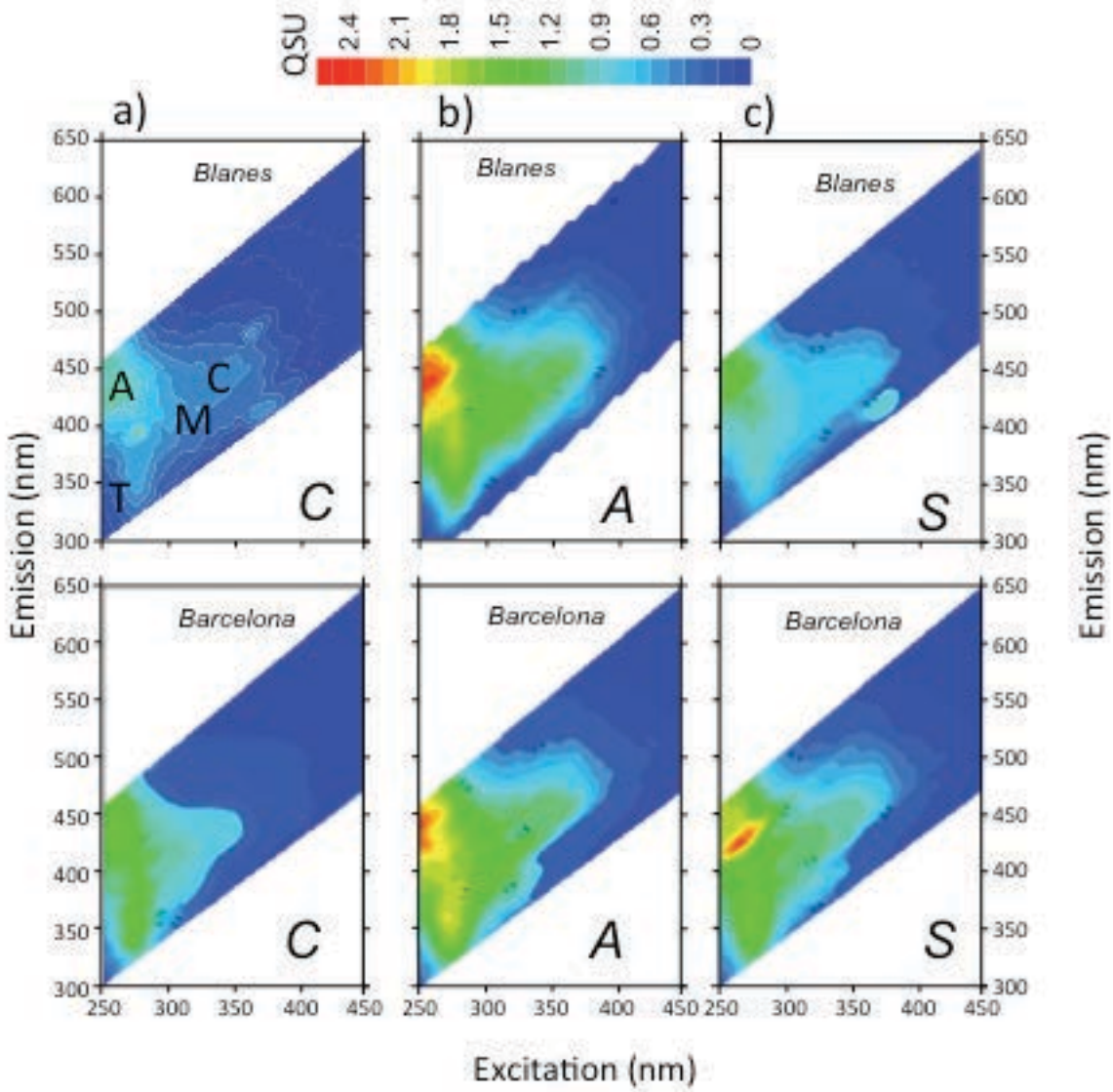

Figure 5. Changes in the excitation-emission matrix (EEM) of FDOM after dust addition for two experiments. The column (a) before addition (C=control), column (b) after dust (anthropogenic (A) and Saharan (S) respectively). The different peaks are indicated. The fluorescence is expressed in quinine sulfate units (QSU).

4. DISCUSSION

4.1. Atmospheric deposition influence in surface waters

Interestingly, the highest FDOM deposition values coincided with the Saharan dust events (Fig. 1). Although CDOM is present in low concentrations in the Mediterranean (Romera-Castillo et al., 2013; Xing et al., 2014), the ratio CDOM to Chla *a* is exceptionally high respect to other areas (Morel & Gentili 2009, Organelli et al., 2014). Because FDOM is a part of the CDOM pool, our observations could indicate that atmospheric inputs during Saharan events could significantly contribute to this high CDOM/Chl *a* ratio. Para et al. (2010) pointed out that the humic fluorescent components and the salinity had an exceptional weak correlation and suggested that other processes could influence CDOM distributions. Thus, our results about FDOM deposition during Saharan events could contribute to explain these anomalies.

4.2. Effects of aerosols additions on the prokaryotic abundances

Previous studies have demonstrated that prokaryotic abundances increased in response to Saharan dust inputs in oligotrophic systems (Pulido-Villena et al., 2008; Reche et al., 2009). However, in our experiments, the prokaryotic response to dust addition was low. In BLSp and BCNSp experiments, a small prokaryotic growth was observed specially in the microcosms enriched with Saharan dust only 4 hours after the addition for BLSp and after 28 hours for BCNSp, whereas the response of chlorophyll took place much later in time. This is in good agreement with the results obtained by Marañon et al. (2010), where a quicker response of prokaryotes was observed in more oligotrophic areas compared with the response of chlorophyll. The contrary occurred in more eutrophic areas (Teira et al., 2013). In general the abundance tended to decrease through the course of the incubations, being this decrease more conspicuous in the enriched treatments than in the control. We attributed this behaviour to the competition for limiting nutrients between phytoplankton and bacteria (Marañón et al., 2010). In any case, the response in both

experiments was lower than expected. In fact, authors as Ridame (2001), Marañon et al (2010) and Herut et al (2005), also found low prokaryotic stimulation to the aerosols inputs in Mediterranean waters. In the BCNSp experiment chlorophyll increased close to 4-fold during the first two days of the experiment independently of the treatment, although the peak observed at day two was more noticeable in the A microcosms. This increase could be, in part, due to the use of nitrate or ammonium that was in the initial water, and the larger response in A conditions could be related to the higher nitrogen and silicon proportions supplied by the anthropogenic aerosols with respect to the Saharan ones (Table I). Differences in the microbial responses seemed to be related with the initial environmental conditions (e.g. nutrient availability). Martinez-Garcia et al. (2015) also pointed out the importance of initial conditions to explain the variety of microbial responses when examining the effect of rainwater additions in experiments performed with NW Iberian Peninsula shelf waters. In our experiments, the quality of the added particles could be another factor explaining the differences in microbial response between the two experiments. Even if the A and S aerosols were collected during non-Saharan and Saharan events respectively, the organic matter composition of the particles differed between experiments, as it will be discussed below.

Table I. Relative percentage of the composition of the different aerosols used in BLSp and BCNSp experiments respectively. Abbreviations: A= anthropogenic, S=Sahara, OC= organic carbon, CO_3= carbon trioxide, SiO_2= silicate oxide, Al_2O_3= aluminum oxide, NO_3^-= Nitrate, NH_4^+= ammonium and P= phosphorus.

	Blanes (BLSp)		Barcelona (BCNSp)	
	A	S	A	S
OC	31.95%	4.93%	26.38%	6.75%
SiO_2	4.75%	40.64%	13.56%	27.88%
Al_2O_3	1.58%	13.55%	4.51%	9.29%
NO_3^-	11.01%	2.48%	7.81%	2.11%
NH_4^+	2.12%	0.37%	1.47%	0.52%
P	0.10%	0.08%	0.13%	0.07%

4.3 DOM optical properties transformations after dust additions

In the BLSp experiment, the humic-like fractions of OM increased after the addition of aerosols, being this increase more conspicuous in the A treatment than in the S. In fact, Peak-C/DOC ratios in QSU/µmol C L^{-1} increased a 153% in A and a 33% in S with respect to the control. However, FDOM compounds did not show a variation through the incubation time, In the BCNSp experiment, FDOM values were also higher after the addition. However the increases in FDOM/DOC ratio after additions were larger in S than in A, 70% and 89% respectively. In both BLSp and BCNSp experiments, we observed that DOC tended to increase in all treatments over the time of incubation, being this increment larger in BCNSp and in BLNSp experiment which is in accordance with a high activity of phytoplankton (Table II). The excitation-emission matrices (EEMs) confirmed that both anthropogenic and Saharan aerosols contained fluorescence organic substances (Fig. 5) as it has been previously reported by Mladenov et al. (2011).

Regarding the fluorescence quantum yield at 340 nm, [Φ(340)], we observed a similar increase in both experiments after the addition was performed, reaching values of about 0.65 % (Fig. 6). The quantum yield decreases with light exposure and increases with microbial activity (Romera-Castillo et al. 2011). Then, the increase in quantum yield values observed after the enrichment could indicate a rapid, although low, bacterial response. In fact, we observed that low values of Φ(340) coincided with low bacterial abundance and vice versa.

The values of Φ(340) obtained in our experiments were within the range of other previously reported data from field studies in the Mediterranean (Ferrari 2000, Romera-Castillo et al. 2011*)*, thus indicating that our induced changes in optical characteristics of organic matter were within the range of variations occurring in nature.

Table II. Concentration chlorophyll in µgr L^{-1} for the different treatments of BLSp and BCNSp experiments at three sampling days: at initial time (t0), final time (144 h and 97 h for BLSp and BCNSp respectively) at the day where the chlorophyll maximum occurred. The day of the maximum is also indicated.

BLSp	Initial	Final	Max	Day-Max
C	0.27 ± 0.01	0.49 ± 0.05	0.51 ± 0.02	6
A	0.31 ± 0.03	0.60 ± 0.05	0.74 ± 0.02	5
S	0.28 ± 0.01	0.52 ± 0.03	0.56 ± 0.01	4
BCNSp	Initial	Final	Max	Day-Max
C	4.75 ± 0.03	0.46 ± 0.1	4.6 ± 0.2	1
A	4.4 ± 0.18	0.48 ± 0.4	6.2 ± 0.04	2
S	4.4 ± 0.03	0.53 ± 0.1	5.2 ± 0.04	2

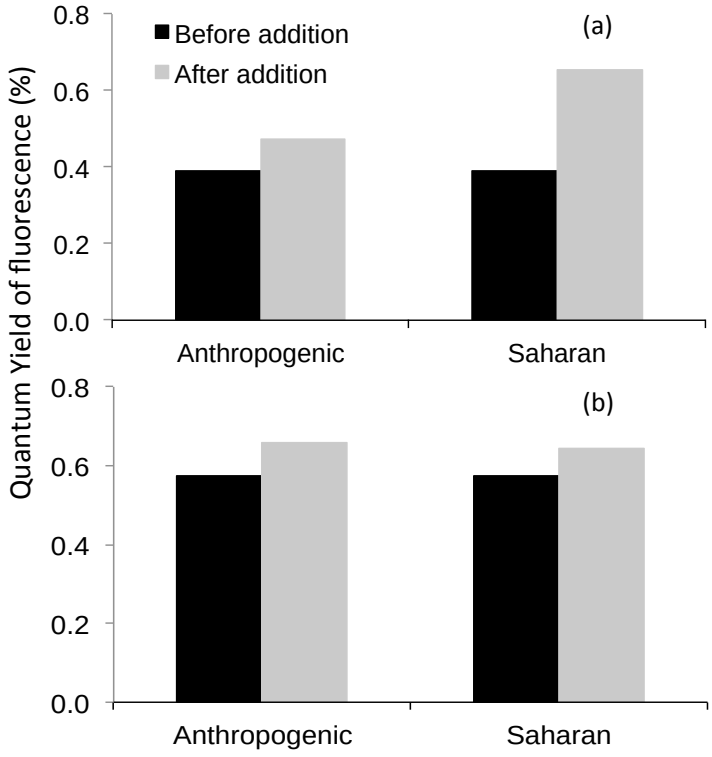

Figure 6. Fluorescence quantum yield at 340 nm [Φ (340)] before-after anthropogenic and Saharan dust addition. (a) BLSp experiment and (b) BCNSp experiment. The [Φ (340)] is expressed in percentage (%).

5. SUMMARY

Our experimental results revealed that aerosols deposition induced an increase in the proportion of FDOM with respect to DOC. An increase of rather refractory organic matter was confirmed by the negligible utilization of this fraction within a short time period (days). The induced increase of the coloured DOC fraction with dust deposition together with the subsequent low utilization could contribute to the exceptional high values of CDOM related to chlorophyll in the Mediterranean Sea.

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CHAPTER V

CONCLUSIONS GÉNÉRALES ET PERSPECTIVES

1. CONCLUSIONS

1.1. Dynamique de la CDOM dans les systèmes côtiers et océaniques

Notre étude s'est focalisée sur l'observation du rôle des facteurs biotiques et abiotiques qui influencent dans la dynamique de la MOD et de ses propriétés optiques (CDOM). Pour atteindre nos objectifs, nous avons étudié deux systèmes contrastés, gouvernés par des facteurs forçants distincts à une station fixe côtière (SOLA) et une station fixe hauturière (MOLA).

La station SOLA est un système principalement contrôlé par l'arrivée d'eau continentale à faible salinité (rivières méditerranéennes telles que la Baillaury, voire la Têt ou le Tech) et par les mélanges liés à la houle. Dans cette zone côtière, nous avons supposé que l'influence anthropique pouvait altérer le système et nous avons alors montré que, contrairement à ce que l'on pourrait s'attendre, les variabilités aussi bien saisonnières qu'annuelles ne montrent pas de tendance à l'augmentation au cours de la dernière décennie.

Nous avons trouvé deux mécanismes principaux qui dominant la dynamique de la MO et de la production biologique. Une augmentation des Pic-C et Pic-M d'environ 1 à 3 fois en hiver par rapport aux valeurs estivales a été mesurée. Ces fortes différences entre l'hiver et l'été sont le résultat de:

(i) l'apport hivernal d'eau douce continentale riche en CDOM : En effet, les apports telluriques modifient significativement la quantité mais surtout la qualité de la CDOM.

(ii) une forte exposition estivale aux rayonnements solaires : En effet, l'apparition puis le renforcement de la stratification au cours de l'été entraîne l'exposition de la MOD à la lumière et favorise ainsi une photo-dégradation entraînant la diminution de l'intensité de fluorescence.

Par conséquent, nous suggérons que photo-blanchiment apparaît comme un important puits alors que les débits fluviaux représentent une source importante de CDOM. En outre, nous suggérons que le dysfonctionnement de la boucle microbienne et la pression de prédation sur les hétérotrophes osmotrophes pourraient expliquer l'accumulation de COD en été; Tous ces processus peuvent être résumés dans la figure 1.

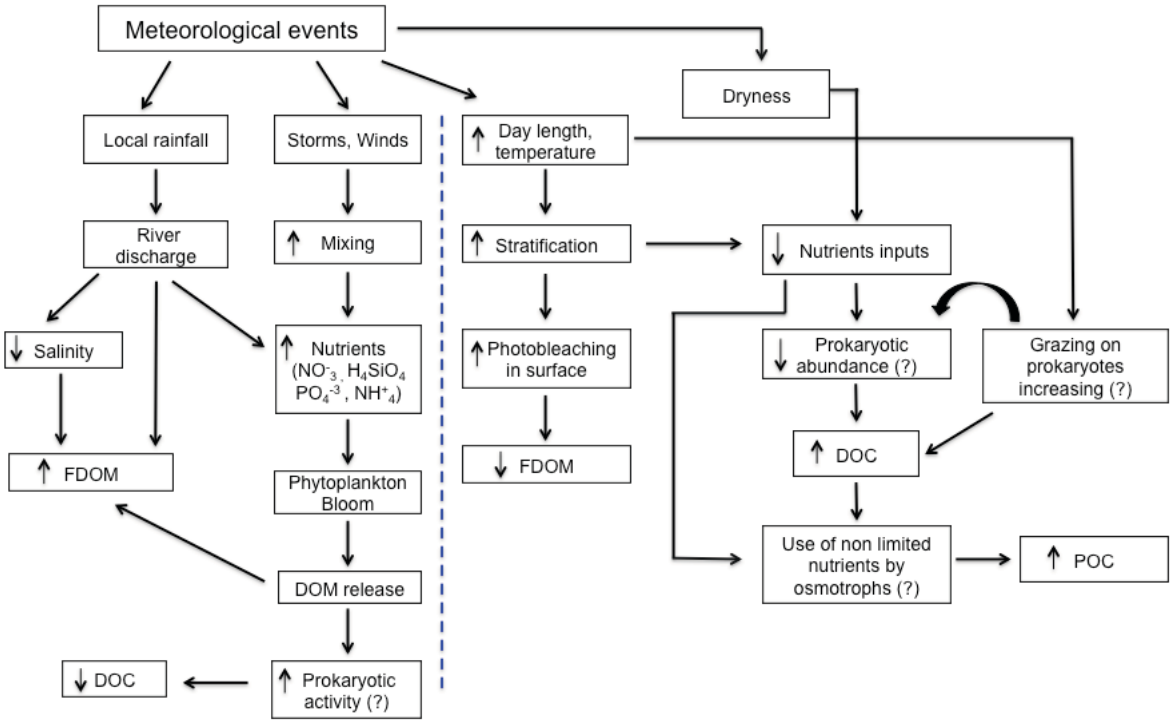

Figure 1. Schéma synthétique de la réponse de l'écosystème côtier aux variations des conditions météorologiques et des processus photochimiques dans la baie de Banyuls-sur-mer (station SOLA). La ligne pointillée bleue sépare les principaux mécanismes survenant en saison estivale (côté droit) de ceux plus épisodiques hivernaux (à gauche). Les flèches vers le haut indiquent une augmentation, celles vers le bas, une diminution. Les points d'interrogation indiquent l'absence de mesures directes pour ces variables.

La station du large MOLA est influencée d'un point de vue physique par la circulation générale (courant Nord Méditerranéen) et par les formations d'eau dense hivernale sur le plateau continental (cascading) et au large (convection thermo-haline). Au cours de notre étude, nous avons échantillonné deux périodes hivernales et une période estivale. L'intérêt est que nous avons rencontré deux conditions très contrastées, avec un hiver marqué par d'importantes formations d'eau dense, suivi par un hiver caractérisé par l'absence de cascading et de convection. Ce constat nous a fourni une base solide pour discuter des variations temporelles de la dynamique de la matière organique dissoute que nous avons observée à la station MOLA.

En effet, le mélange convectif intense de l'hiver 2013-2014 entraîne au printemps, des concentrations en FDOM et COD faibles et homogènes sur toute la colonne d'eau. En revanche, au printemps 2014, les concentrations en DOM et en FDOM étaient relativement plus élevées dans la couche de surface, suite à l'absence d'homogénéisation poussée en hiver. Au cours de l'été, l'exposition au rayonnement solaire liée à la présence de la stratification thermique entraîne la diminution de l'absorption et de fluorescence suite au phénomène de photo-blanchiment des substances humiques (diminution de l'aromaticité) et ceci, d'autant plus que les concentrations initiales sont importantes.

Par conséquent, cette étude met en évidence que la production "in situ" est la source principale et le photo-blanchiment apparaît comme un puits majeur de CDOM dans les eaux océaniques. La variabilité des propriétés optiques de la DOM a été contrôlée principalement par les processus physiques. Ces processus impliqués dans la dynamique de la DOM à la station MOLA sont synthétisés dans la figure 2.

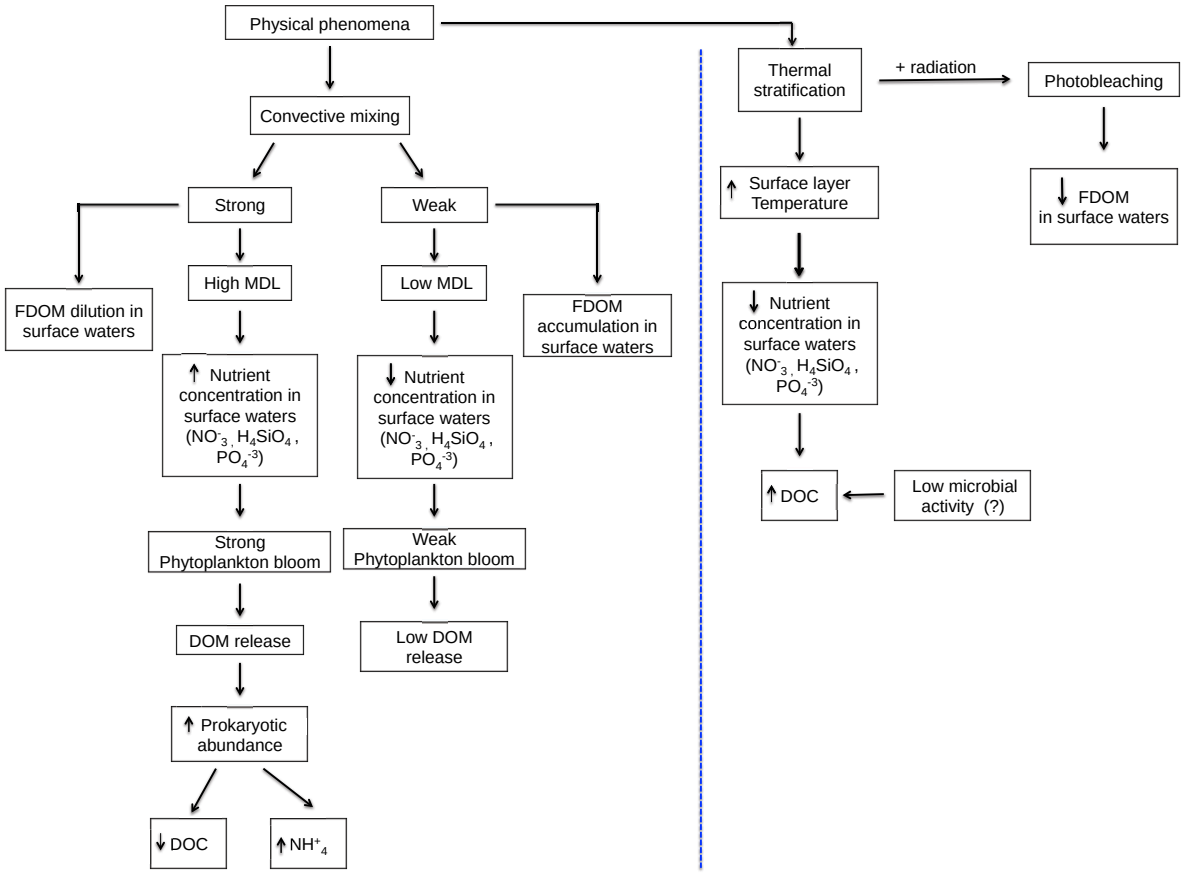

Figure 2. Schéma synthétique de la séquence des différents phénomènes physiques impliqués dans la dynamique de DOM dans un écosystème hauturier (station MOLA). La ligne pointillée bleue sépare les principaux mécanismes survenant en saison estivale (côté droit) de ceux plus épisodiques hivernaux (à gauche). Les flèches vers le haut indiquent une augmentation, celles vers le bas, une diminution. Les points d'interrogation indiquent l'absence de mesures directes pour ces variables.

1.2. Source atmosphérique de FDOM

A notre connaissance, les apports atmosphériques de DOM dans les écosystèmes marins ont été très peu évalués. Pour déterminer la contribution relative des dépositions atmosphériques dans la dynamique de la CDOM, en termes de stock, propriétés et comme stimulant de l'activité microbienne, nous avons réalisé deux expériences en domaine côtier, en utilisant des mésocosmes alimentés en eau de mer naturelle et enrichis à l'aide de poussières provenant de différentes sources (régions de Barcelone et Blanes). Ces résultats expérimentaux font partie du projet ADEPT "CTM2011-23458" (PI : Dr. Cèlia Marrasé).

Quelle que soit l'origine de l'eau de mer utilisée dans les essais expérimentaux, nous avons trouvé une augmentation de la proportion de FDOM par rapport au COD après ajout des poussières. Nous avons pu montrer que cette augmentation correspondait à de la matière organique plutôt réfractaire comme le prouve la faible utilisation de la MO par le compartiment bactérien. Cette augmentation de la DOM colorée avec les dépositions atmosphériques et sa faible utilisation par le compartiment microbiologique pourraient expliquer en partie les valeurs exceptionnellement élevées de CDOM liées à la chlorophylle signalées parfois dans les eaux de la mer Méditerranée.

En résumé, les facteurs biotiques et abiotiques, ainsi que les phénomènes physiques impliqués dans la dynamique de la matière organique, dans cette étude sont représentés dans la figure 3 et 4.

(a)

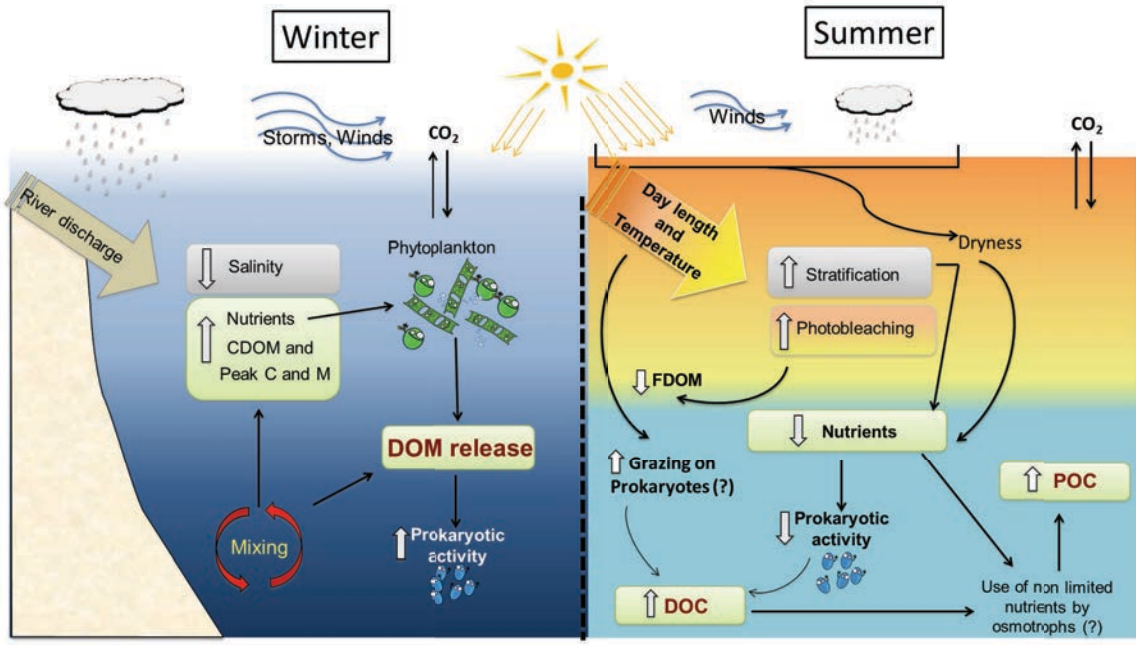

Figure 3. Facteurs biotiques et abiotiques contrôlant la dynamique de la CDOM en Baie de Banyuls sur-mer (station SOLA) pendant (a) la période hivernale et (b) la période estivale.

(b)

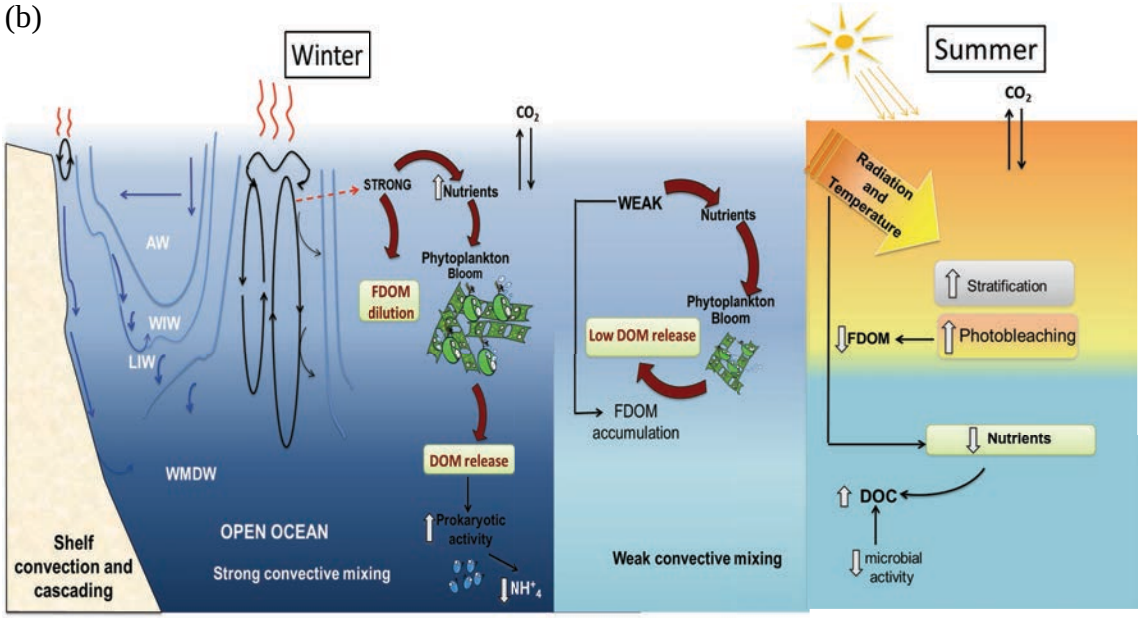

Figure 4. Facteurs biotiques et abiotiques contrôlant la dynamique de la CDOM dans le golfe du Lion (station MOLA) pendant (a) la période hivernale (physique dominée par les processus de convection) et (b) la période estivale (stratification).

2. PERSPECTIVES

Ce travail est une première approche du rôle des facteurs biotiques et abiotiques dans la dynamique de la MO et son influence sur la biogéochimie de la région. Nous avons apporté des éléments importants pour la compréhension du fonctionnement et de la variabilité temporelle à différentes échelles des eaux marines aussi bien côtières que hauturières de la Mediterranée.

Il serait nécessaire de poursuivre la quantification et la caractérisation de la MOD dans les sources continentales, notamment pour vérifier si les différentes rivières (par exemple, Baillaury, Têt, Tech ou Rhône) présentent des signatures équivalentes en termes de CDOM/FDOM. Il faudrait également valider nos hypothèses sur la dynamique de la MOD, en confrontant nos résultats à d'autres régions côtières influencées ou non par des apports continentaux (région de Marseille et en mer Ligure par exemple en utilisant le suivi SOMLIT). L'augmentation de la fréquence d'observation est également une piste à privilégier (mise au point de technique de mesures en continu).

A la station MOLA, il est nécessaire de poursuivre l'échantillonnage de la CDOM couplé au suivi de l'activité microbienne (production primaire et production bactérienne). En effet, seule cette approche développée en collaboration avec des équipes de modélisateurs devrait nous permettre de confirmer ou d'infirmer nos hypothèses sur l'importance des phénomènes physiques tels que le mélange convectif. En outre, cela permettrait de suivre l'accumulation et la transformation du DOC au cours de la stratification dans les couches superficielles, puis son export vers les couches profondes.

Enfin, nous avons montré que les dépositions atmosphériques ont un impact important sur la qualité et la quantité des propriétés optiques de la CDOM disponibles dans les eaux de surface. Il faut élargir ces observations à d'autres zones et préciser la composition élémentaire des poussières, ainsi que leur devenir dans d'autres types d'écosystèmes afin d'expliquer pourquoi ces poussières ne stimulent pas l'activité microbienne.

Cela pourrait se faire dans le cadre du chantier MISTRALS et de l'évolution de la composante MERMEX. L'une des voies actuellement en discussion concerne le GOEAST, c'est-à-dire appliquer les stratégies utilisées au cours de l'expérience DEWEX au bassin oriental et aux plongées d'eau dense à l'origine de la formation des eaux profondes orientales.

Pour finir, notre objectif est d'élargir nos observations à d'autres zones car la Méditerranée constitue un écosystème à part par rapport aux autres systèmes océaniques. A notre connaissance, peu d'études existent sur le rôle de la matière organique dissoute dans l'écosystème marin des eaux mexicaines. J'envisage de proposer une étude ciblée dans les eaux de la Basse Californie (Pacifique Nord). Il s'agira d'étudier le rôle de la CDOM liée aux phénomènes physiques caractéristiques de la zone (phénomènes contrastés d'el Niño et de la Niña). Les dynamiques et les transformations de la CDOM au cours des phénomènes et de la transition entre les périodes de Niño/Niña sont essentielles à connaitre pour comprendre le bilan du fonctionnement biogéochimique de la zone et son rôle dans le contrôle des productions primaire et bactérienne. Cela pourrait se faire dans le cadre du chantier IMECOCAL (Investigaciones Mexicanas de la Corriente de California). Le projet IMECOCAL développe un programme de recherche dans le secteur sud du courant de Californie, qui comprend un plan d’échantillonnage dans eaux océaniques et au large de la Basse Californie. L'échantillonnage sera effectué quatre fois par an (automne, hiver, printemps et été). Ce projet est financé par plusieurs organismes mexicains et étrangers.

ANNEXES

1. CONCLUSIONS

1.1 CDOM dynamics in coastal and oceanic system

Our study focused on examining the role of biotic and abiotic factors that influence the dynamics of DOM and its optical properties. To achieve our objectives we investigate two contrasting systems governed by distinct driving forces in a coastal station (SOLA) and in an oceanic site (MOLA).

SOLA station is located in an oligotrophic system that mostly is controlled by the input of low salinity water from rivers e.g. Baullaury, Têt and Tech and also by the occurrence of swells. In this coastal area, we assumed that anthropogenic influence could alter the system and we showed that, contrary to that you might expect, both seasonal and annual variability did not find any reductio with time.

We found an increase of Peak-C and Peak-M of about 1-3-fold in winter respect to the summer values. We suggest two mechanisms to explain these high differences:

(i) The input of fresh water in winter, which is rich in CDOM: In fact, the terrestrial inputs significantly alter the quantity but also the quality of CDOM.

(ii) The stratification and high sunlight exposure in summer favour the photo-degradation of organic matter and thus the decrease in fluorescence intensity.

Therefore, we suggest that photo-bleaching appears as a major CDOM sink whereas the river discharges represent an important source of CDOM. In addition, we suggest that both the malfunction of microbial loop and the predation pressure on heterotrophic osmotrophs could explain the DOC accumulation in summer; all processes can be summarized in the Figure 1.

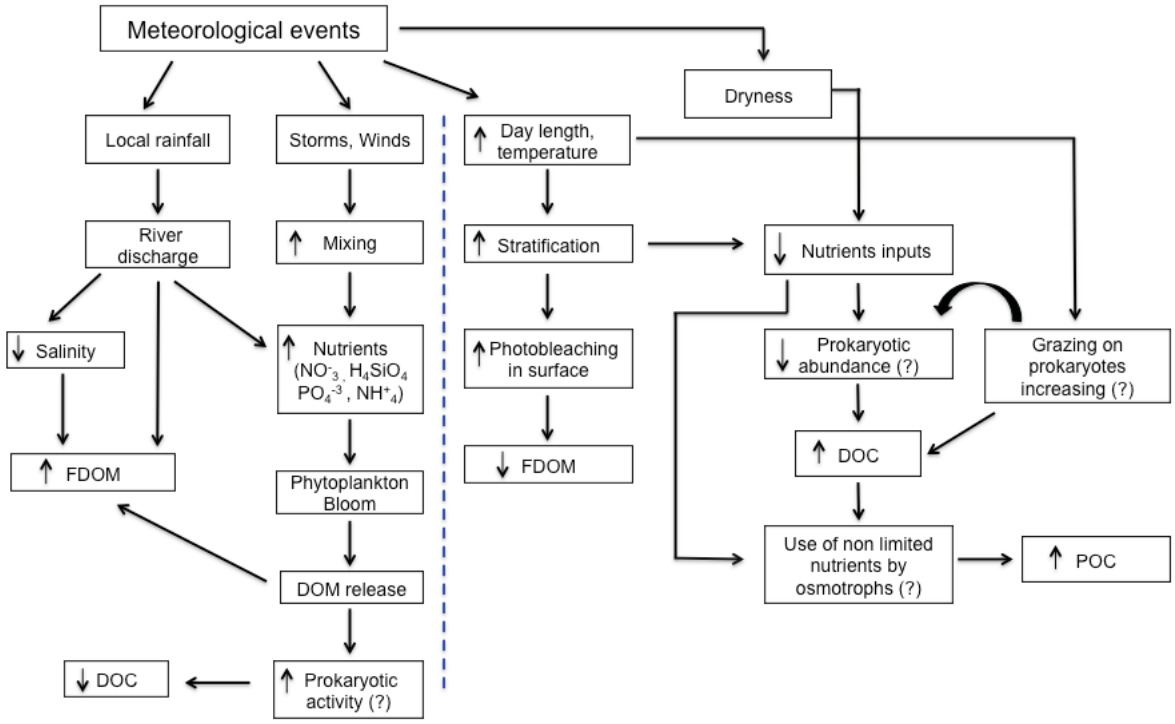

Figure 1. Synthetic scheme of the coastal ecosystem response to meteorological events and photochemical processes in the Bay of Banyuls-sur-mer (SOLA station). The discontinuous line separates the principal mechanisms occurring in summer season (right side) from those more episodic ones operating in winter (left side). The arrows up indicate an increase, and the arrows down a diminution. With question marks we indicate the variables for which we do not have data but we do have indirect evidence to hypothesize that these variables or mechanisms play a role in the dynamics of organic matter.

The offshore station MOLA is influenced, from a physical point of view, by the general circulation (current North Mediterranean), particularly by the formation of the dense water on the continental shelf (cascading) and offshore (thermohaline convection). During our survey period we monitored two winter periods and one summer period. We found two contrasting winter conditions; the first one (2013) was marked by significant dense water formations, while the second winter (2014) was characterized by the absence of cascading and convection. This contrast has provided a solid base to discuss the temporal variations of the dynamics of dissolved organic matter that we observed at the MOLA station.

In fact, the intense convective mixing in winter during 2013-2014 led to low and homogenous concentrations of DOC and FDOM throughout the water column. In contrast, in spring 2014 both DOC and FDOM values were relatively higher in surface layer. In warm periods, the high solar radiation exposure during thermal stratification produced a decrease of absorption and fluorescence due to the photo-bleaching of the humic-like substances (decrease the aromaticity).

Therefore, this study evidences that the “in situ” production is the main source and photo-bleaching is the major sink of CDOM in oceanic waters. Physical processes described above governed the variability of optical properties of DOM. The involved processes in the dynamics of DOM to MOLA station are summarized in Figure 2.

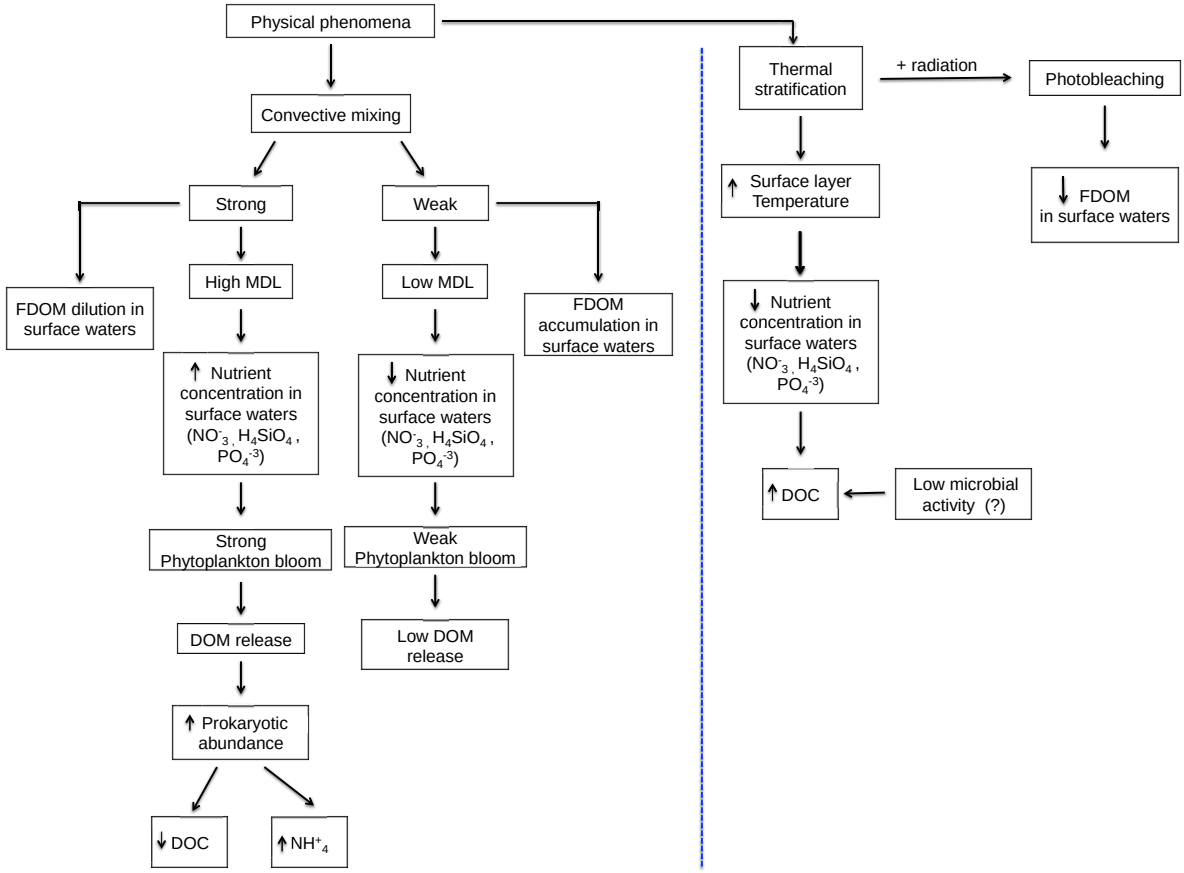

Figure 2. Synthetic scheme showing the sequence of the different physical phenomena driving the DOM dynamics in an ocean ecosystem (MOLA station). The discontinuous line separates the principal mechanisms occurring in summer season (right side) from those ones more episodic operating in winter (left side). The arrows up indicate an increase, and the arrows down a diminution. With question marks we indicate the variables for which we do not have data.

1.2 . Atmospheric source of FDOM

To our knowledge, DOM atmospheric inputs in marine ecosystems have been feebly evaluated. To determine the relative contribution of atmospheric depositions in the dynamics of CDOM in terms of stock, optical properties, and its influence on microbial activity, we conducted two experiments in two different sites (Barcelona and Blanes) of the Catalan coast, using mesocosms supplied with natural seawater enriched with dust from different sources (Saharan and urban).

Regardless of the origin of the seawater used in the experiments we found an increase in the proportion of FDOM respect to DOC after dust additions. We showed that this increase corresponds to rather refractory organic material, this refractory character being confirmed by the low posterior utilization of the OM. The induced increase of colored DOM fraction with dust deposition together with the posterior low utilization could contribute to explain the exceptional high values of CDOM related to chlorophyll reported in the Mediterranean Sea waters.

In summary, the biotic and abiotic factors and physical phenomena involved in the dynamics of organic material, in this study are shown in the figure 3 and 4.

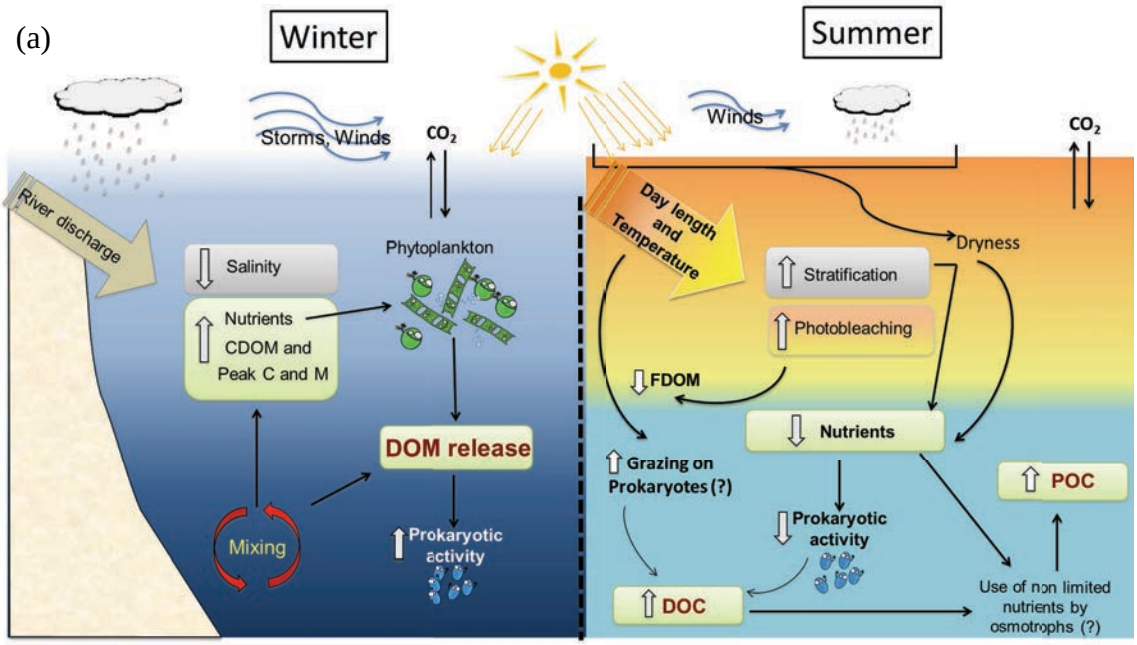

Figure 3. Biotic and abiotic factors controlling the dynamics of CDOM in the Bay of Banyuls sur Mer (SOLA station) for (a) winter period and (b) summer period.

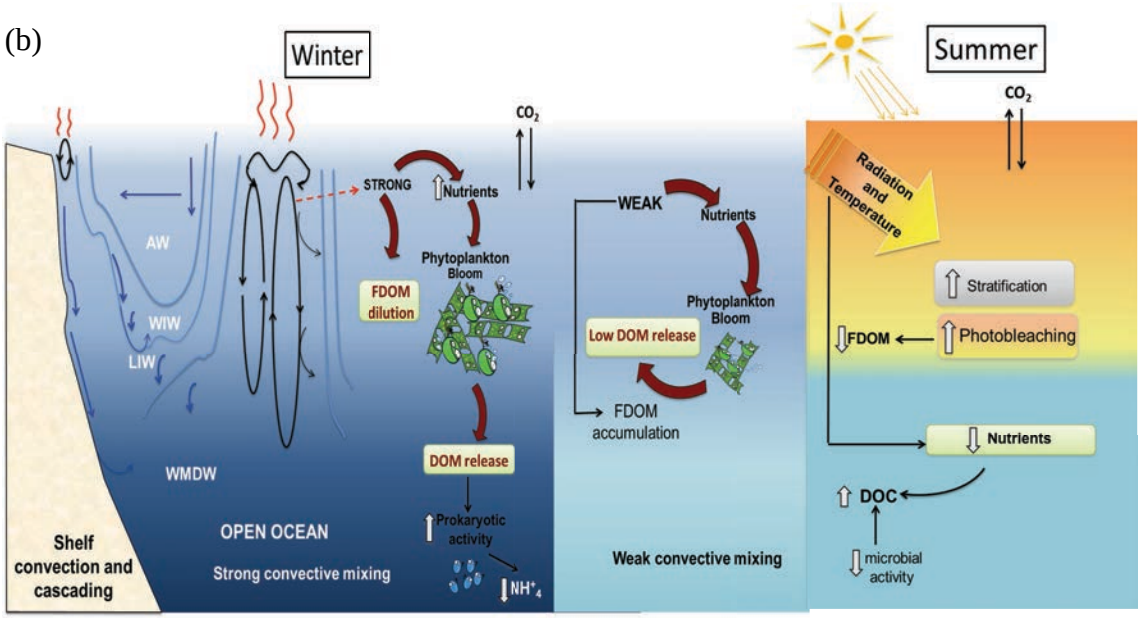

Figure 4. Biotic and abiotic factors controlling the dynamics of CDOM in the Gulf of Lion (MOLA station). (a) winter period (physic dominate by convective mixing) and (b) summer period (stratification).

2. PERPECTIVES

This work allowed us to perform a first approach about the role of biotic and abiotic factors in the organic matter dynamics and its influence on the biogeochemistry of the Mediterranean region. We provided new insights about the functioning and temporal variability at different scales in the marine waters as well as coastal seas.

It would be necessary to continue the quantification and characterization of the DOM in continental sources to verify whether or not if various rivers (e.g. Baillaury, Têt, Tech or Rhône) have equivalent signatures in terms of CDOM / FDOM. Additional data would also validate our assumptions about the dynamics of DOM, and would allow us to compare our results with others coastal regions, which receive or not continental inputs (Marseille region and Ligurian Sea, for example using the SOMLIT monitoring). Simultaneous sampling for physical, chemical and biological variables at high frequency of observation would be crucial for a better understanding of CDOM dynamics in coastal areas (e.g. buoys with sensors for continuous measurements).

At the MOLA station we propose to continue the CDOM sampling, this, combined with microbial activity (primary production and bacteria production) monitoring. In fact, this approach together with modeller's collaboration would be decisive to corroborate or refute our hypotheses about the importance of physical phenomena such as convective mixing in driving the organic matter dynamics. Also, it would permit to examine the accumulation or transformation of DOC during the period of stratification in the surface layers and its possible export to the deeper layers.

Finally, we showed that atmospheric depositions have an important impact on the quality and quantity of the optical properties of CDOM available in surface waters. We must extend these observations to other areas and identify the elemental composition of the dust, as well as their fate in other types of ecosystems to explain why, in our experiments, the dust did not stimulate microbial activity.

This could be done through the projects Mistrals and MERMEX. One of the paths nowadays in discussion concerns to GOEAST, which applyes strategies used in the DEWEX experiments to the oriental basin and, in particular, to the dense waters immersions.

Finally, our goal is to extend our observations to other areas because the Mediterranean is a separate ecosystem compared with other oceanic systems. To our knowledge, few studies exist about the role of dissolved organic matter in the marine ecosystem of the Mexican waters. We propose a study in the waters of Baja California (North Pacific), in which we will study the role of CDOM related to physical characteristic phenomena of the area (e.g. phenomena El Niño and La Niña). The dynamics and transformations of CDOM through these phenomena and its transition between periods of El Niño / La Niña are essential to understand the balance between the biogeochemical functioning of the area and its role in controlling primary and bacterial production. This type of study could be performed through the IMECOCAL project (Investigaciones Mexicanas de la corriente de California). This project is funded by several Mexican and foreign organizations and it is developing a research program in the southern sector of the California current, which includes a seasonal sampling in ocean waters, offshore Baja California.

Comunications scientifiques

E. D. Sánchez-Pérez, P. Conan, C. Marrasé, M. Pujo-Pay. Variabilité saisonnière de la matière organique dissoute colorée en zone mediterranéenne côtière. Présenté au congrès CIESM, Marseille, Octobre 2013.

E. D. Sánchez-Pérez, I. Marín, S. Nunes, M. Estrada, F. Peters, M. Pujo-Pay, P. Conan, C. Marrasé. Fluorescent organic matter dynamics induced by inputs of different types of dust. An experimental approach. Présenté au congrès ONE PLANET, ONE OCEAN (2nd International Ocean Research Conference). Novembre 2014.

E.D. Sánchez- Pérez, M. Pujo-Pay, P. Conan, C. Marrasé. Temporal variability of CDOM fluorescence in a coastal station (NW Mediterranean). Présenté au crongrès Aquatic Sciences Meeting (ASLO). Fevrier 2015.

6906 Variabilité saisonnière de la matière organique dissoute colorée en zone meditérranéenne côtière

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INTRODUCTION

La matière organique dissoute colorée (CDOM) joue un rôle clé dans la régulation de la pénétration de la lumière dans l'océan (Fig. 1), en absorbant une partie des ondes électromagnétiques à forte énergie du spectre (visible et rayonnement ultraviolet). D'un côté, cela protège les organismes aquatiques d'un risque de photo-dégradation, mais d'un autre côte cette énergie n'est plus disponible pour la photosynthèse (1, 2). Une fraction de la CDOM émet une fluorescence bleue quand elle est irradiée par des UV, cette fraction est appelée matière organique dissoute fluorescente (FDOM) (3, 4).
Cette étude apporte des informations quant à l'origine et à la dynamique de la FDOM dans les écosystèmes marins côtiers méditerranéens.

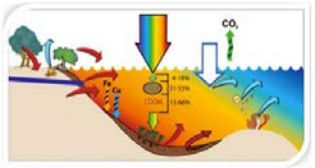

Figure 1. Diagramme conceptuel des possibles sources (flèches rouges), et puits (flèches bleues) de CDOM en milieu côtier d'après Beever (2007) (5).

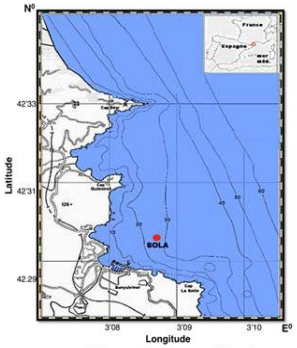

Figure 2. Zone d'étude

MATÉRIELS ET MÉTHODES

Suivi multiparamétrique de 8 mois (mars-novembre 2012) à la station côtière SOLA (Fig. 2)

✧FDOM : Fluorescence mesurée après filtration (0.2 *µM*) à l'aide d'un fluorimètre (Jasco FP2020 +)

✧Mesures ponctuelles aux longueurs d'onde excitation-émission 370-450 et 370-500

Unités données en concentration de quinine sulfate après étalonnage

Existe- il une relation entre les cycles saisonniers des principaux descripteurs de l'écosystème et celui de la CDOM ?

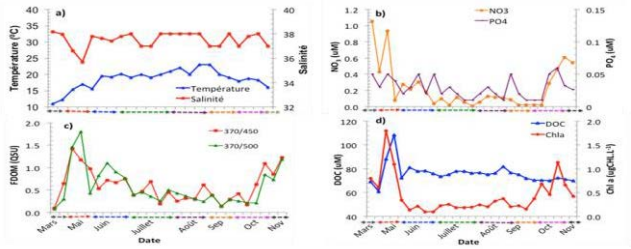

Figure 3. Evolution temporelle de a) Salinité et Température (°C), b) concentrations en nitrate (NO_3) et phosphate (PO_4) en µM ; c) FDOM (QSU) et d) Chlorophylle a (Chla en µgChl.L^{-1}) et carbone organique dissous (DOC en µM)

RÉSULTATS ET CONCLUSIONS

→ Le suivi couvre la totalité de la saison estivale depuis de l'hiver 2012 jusqu'à l'automne 2012 (Fig. 3a). Une forte variabilité à méso échelle se superpose aux variations classiques des sels nutritifs du fait de la position côtière de la station (Fig. 3b). Les concentrations en Chla caractérisent clairement les blooms printanier (>1.5 µg Chl.l^{-1}) en avril et automnal (<1.5 µgChl.l^{-1}) en octobre (Fig. 3d).

→ La variabilité de la concentration en DOC (Fig. 3d) est surtout marquée par le bloom printanier (excrétion de matière labile facilement accessible pour les communautés bactériennes). Les concentrations sont relativement stables le reste du suivi.

→ Contrairement au DOC, les concentrations en FDOM (Fig. 3c) sont caractérisées par une forte variabilité à méso échelle qui intègre selon les composants (couples EX-EM) la dynamique des compartiments physique (apport d'eau dessalée et photo-dégradation estivale), minéral et biologique (apport et consommation des sels nutritifs, bloom algal et consommation bactérienne).

En conclusion, la CDOM et plus précisément sa composante FDOM est un descripteur particulièrement pertinent des processus qui affectent l'organisation et la dynamique des écosystèmes côtiers méditerranéens

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FLUORESCENT ORGANIC MATTER DYNAMICS INDUCED BY INPUTS OF DIFFERENT TYPES OF DUST. AN EXPERIMENTAL APPROACH

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INTRODUCTION

- A fraction of colored dissolved organic matter (CDOM) emits light when excited by UV radiation. This fraction is named FDOM (fluorescent organic matter). Fluorometric analyses allow us to map Excitation-Emission matrix (EEM-Fig.1) and characterize emission peaks that can be used as proxies for lability and origin of the organic matter.
- Surface waters of NW Mediterranean coast are characterized for its low nutrient and DOM concentration. Recently, a decrease of seasonality in this area have been attributed to water and atmospheric anthropogenic disturbances (Romero *et al* 2014). However little is now about the impact of dust deposition on the quality of DOM.

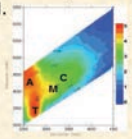

Fig1. Typical Excitation-Emission Matrix (EMM) of surface Mediterranean sea water. Characters indicate the location of the main fluorescence peaks (see text below).

OBJECTIVES

- To examine the impact of contrasting type of dust deposition on the quality of DOM.
- To test the importance of initial water conditions on the FDOM dynamics following dust events.

METHODOLOGY

Fig 2. Location of sampling sites in Barcelona and Blanes Bay (left) and Experimental design (right).

- We performed three experiments : on in winter (Exp. I) and two in spring (Exp. II & III). Water was collected at two sites (Fig. 2): Barcelona coast (Exp. I & III) and Blanes Bay (Exp. II) and distributed in six microcosms and incubated for four to six days with controlled light and temperature levels mimicking *in situ* conditions. Two microcosms were enriched (0.8 mg L^{-1}) with Anthropogenic dust (A), two other with Sahara dust (S), and two were kept as control (K). See more details about the experimental design in Marín *et al* 2014.
- Using a combination of different pairs of excitation-emission [EX(nm)/EM(nm)] wavelengths we determine different types of FDOM: Peak-A (250/435), Peak-C (340/440) and Peak-M (320/410) humic-like compounds, and Peak-T (280/350) protein-like substances according to Coble (1996).
- Peak T is used as a proxy of fresh DOM production and Peak M as a proxy of respiration (Romera-Castillo *et al* 2011).
- The fluorescence quantum yield at 340 nm is the portion of the light absorbed at 340 nm that is re-emitted as fluorescent light. In this study it was used as a proxy for recalcitrant DOM.

RESULTS

Dust impact on FDOM

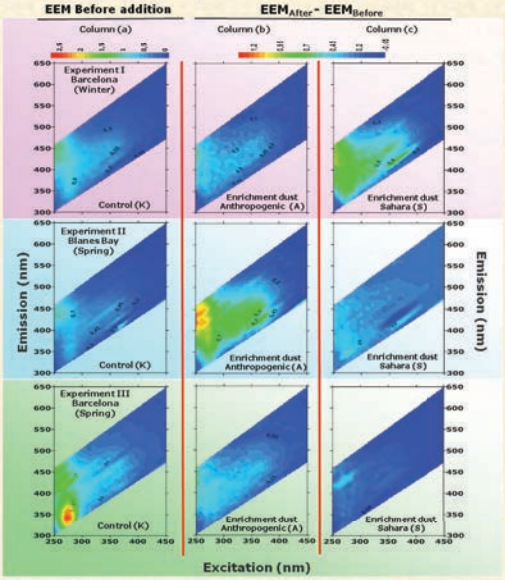

Fig 3. Changes in FDOM after dust addition for the 3 experiments. Column (a) EEM before addition. Column (b) and (c) Represent the subtraction of the EEM before from after dust addition of Anthropogenic and Sahara respectively. Expressed in quinine sulfate units (QSU).

Fluorescence quantum yield (Φ_{340}) after dust addition

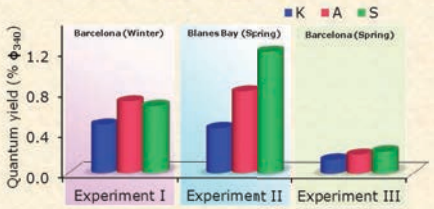

Fig 4. Fluorescence quantum yield at 340 nm after Anthropogenic (A) and Sahara (S) dust addition respectively. Expressed as a percentage (%). K was kept without addition.

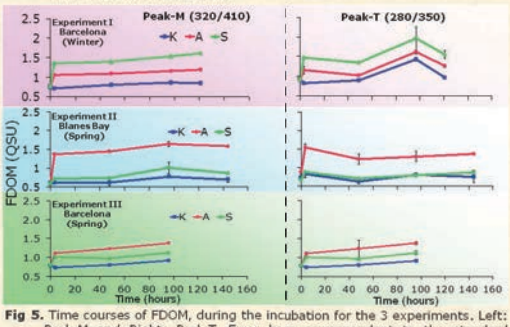

Fig 5. Time courses of FDOM, during the incubation for the 3 experiments. Left: Peak-M and Right: Peak-T. Error bars correspondent to the standard deviation.

CONCLUSIONS:

- Both Anthropogenic and Sahara dust contain fluorescence organic substances. Quality and quantity of this FDOM (relative to dry weight) varied depending on the collection period (Fig.3).
- Low quantum yield values found for FDOM dust indicate low lability of the airborne organic substances (Fig. 4).
- No significant changes were observed during the incubation time, this also indicates a low lability of the added FDOM (Fig.5).

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TEMPORAL VARIABILITY OF CDOM FLUORESCENCE IN A COASTAL STATION (NW MEDITERRANEAN)

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INTRODUCTION

A fraction of dissolved organic matter (DOM) that absorbs at both UV and visible wavelength is referred as colored dissolved organic matter (CDOM), and a small portion emits light when excited by UV radiation. This fraction is called fluorescent DOM (FDOM, Fig. 1a). Fluorometric analyses allow us to map Excitation-Emission matrix (EEM-Fig.1b) and to characterize FDOM emission peaks that can be used as proxies for lability and origin of the organic matter.

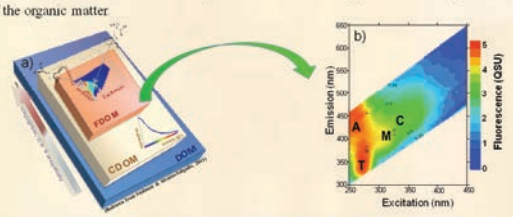

Figure 1. a) Scheme of optically active DOM fractions and b) Typical Excitation-Emission Matrix (EMM) of surface Mediterranean sea water. Characters indicate the location of the main fluorescence peaks (see text below).

OBJECTIVE

To evaluate the influence of abiotic and biotic factors on the temporal dynamics of DOM.

RESULTS

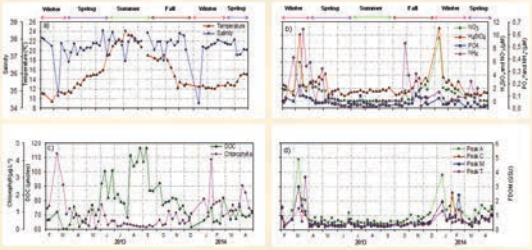

Figure 3. Temporal variability of physical and chemical parameters in SOLA station from Winter 2013 to Spring 2014. a) Temperature & Salinity; b) Inorganic nutrients (NO_3, H_4SiO_4, PO_4^{-3}, and NH_4^+); c) Chlorophyll & DOC and d) Fluorescence dissolved organic matter (FDOM).

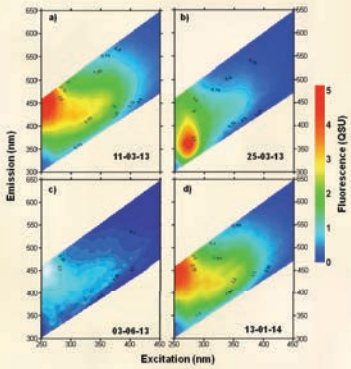

Figure 4. a) Excitation-Emission matrices (EEMs) of the FDOM produced in SOLA station of four samples representative of contrasting hydrological conditions during sampling period: a) & b) Intrusion of water of low salinity; c) Photo-bleaching period, and d) Convective mixing. The color bar indicates the fluorescence intensity expressed in quinine sulfate units (QSU).

METHODOLOGY

Figure 2. Map of the study area in Bay of Banyuls sur-Mer, NW Mediterranean Sea, the red circle indicates the location of the sampling station (SOLA).

- We performed a multi-parameter sampling in a coastal station (SOLA), located at the Bay of Banyuls sur-mer. SOLA station was sampled weekly during 14 months. Seawater samples were collected at 3 m depth for physical and chemical parameters (T, S, Nutrients, Chla and DOC).
- Using a combination of different pairs of excitation-emission [EX(nm)/EM(nm)] wavelengths we determined different types of FDOM. Peak-A (250/435) humic-like substances, Peak-C (340/440) terrestrial-like substances, Peak-M (320/410) marine-like substances, and Peak-T (280/350) protein-like substances according to Coble, (1996).

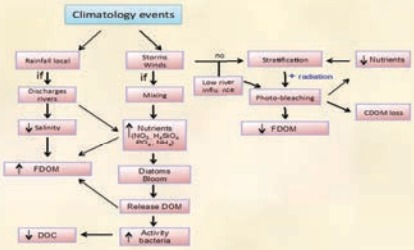

Figure 5. a) Hypothetical scheme of response to climatology events and photochemical process in the station SOLA.

CONCLUSIONS

- The highest concentrations of FDOM humic-like substances coincided with decreases of salinity indicating a notable fresh-water contribution to the organic matter pool.
- The lowest intensity fluorescence and low contribution of FDOM humic-like and protein-like substances was found from spring to early-fall likely due to photo-bleaching processes occurred during the stratification (Coble, 2007; Para et al., 2010).
- DOC concentrations showed its maxima in late spring and summer due to a low bacterial activity associated to nutrient limitation, but these maxima did not coincide with the FDOM peaks as we could anticipate due to the photo-lability of FDOM substances.
- All humic FDOM-peaks showed a significant positive correlation with Nitrates and Silicates and negative with DOC, temperature and salinity, and the canonical correlation analysis (not shwon) confirms that the supply of nutrients was principally due to river discharge (Têt, Tech and Rhône) from January to April.

Acknowledgments

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RÉSUMÉ

Rôle des mécanismes abiotiques dans les dynamiques de la matière organique dissoute dans les écosystèmes pélagiques (Méditerranée Nord occidentale)

La matière organique dissoute chromophorique (CDOM) est une fraction significative du pool global de matière organique dissoute (MOD) dans les océans. La CDOM absorbe une partie de la lumière dans le domaine du rayonnement ultraviolet (UV-R) et du visible. Une fraction de cette CDOM peut émettre une fluorescence lorsqu'elle est excitée par un UV-R. Cette fraction est alors appelée matière organique dissoute fluorescente (FDOM). La CDOM a donc d'une part, un effet positif, en protégeant les cellules contre les dommages causés par les UV-R, mais d'autre part, un effet négatif en réduisant la quantité de radiation disponible pour la photosynthèse.

Les propriétés optiques de la CDOM, particulièrement sensibles aux processus physiques (abiotiques) et biologiques (biotiques), renseignent sur l'intensité des processus biogéochimiques en milieux aquatiques. Des suivis de la dynamique de la CDOM en zones côtière et hauturière en Méditerranée Nord occidentale ont permis de décrire différentes tendances temporelles claires, qui vont d’une faible à une forte saisonnalité et qui peuvent être découplées des variations du pool global de MOD caractérisé par les concentrations en carbone organique dissous (COD). Dans les zones tempérées, les événements météorologiques conduisent à des changements beaucoup plus brusques dans la frange littorale que dans l’océan, où les variations tendent à être plus progressives au cours de l'année. En outre, l'apport de nutriments et de polluants dans les zones côtières est fortement influencé par l'activité anthropogénique et ces entrées ne suivent pas nécessairement de tendances saisonnières nettes.

Dans la présente étude qui effectue un premier bilan de la distribution et du devenir de la CDOM/FDOM aux stations d'observation à long terme du laboratoire Arago (stations côtière SOLA et hauturière MOLA) à partir respectivement d'un suivi hebdomadaire et mensuel, nous nous sommes attachés à extraire un signal cohérent et une variabilité claire des sources des différentes fractions de la MOD entre février 2013 et avril 2014 ceci, de manière à mieux comprendre les rôles respectifs des facteurs biotiques et abiotiques. Nos observations ont ensuite pu être replacées dans un contexte synoptique d'évolution climatologique des écosystèmes méditerranéens.

Dans la zone du golfe du Lion, les nutriments et la chlorophylle ont des variations saisonnières classiques pour une zone tempérée avec une période hivernale marquée par un enrichissement des couches superficielles en sels nutritifs donnant naissance à un bloom printanier plus ou moins précoce selon les zones. L'été est marqué par l'apparition de conditions oligotrophes de plus en plus marquées avec l'avancée de la saison jusqu'à la rupture de la stratification en automne. De façon surprenante, les différentes fractions de la MOD ne montrent pas de tendance

temporelle claire alors que de COD présente une plus forte variabilité en été (accumulation en surface). Pour expliquer ce décalage, nous proposons une séquence de phénomènes abiotiques et biotiques qui forceraient la dynamique de la MOD.

Dans le cadre conceptuel proposé, les facteurs biologiques sont dominants en été, alors que pendant le reste de l'année, la dynamique de la MOD dépend fortement d'événements météorologiques (tempête, cascading). Afin de préciser l'influence des facteurs biologiques sur la distribution de la FDOM, nous avons suivi l'influence du développement et de la composition des blooms phytoplanctoniques sur la dynamique de cette FDOM aux différents sites étudiés. Nos observations indiquent que les facteurs abiotiques tels que les intrusions d'eau dessalée et/ou l'exposition aux radiations solaires sont dominants par rapport à la variabilité des communautés phytoplanctoniques.

De façon complémentaire à ces études de terrain, nous utilisons la base de données de déposition de poussière de projet ADEPT (ICM-CSIC, Barcelone) pour étudier le rôle potentiel du déposition atmosphérique dans la variabilité temporelle CDOM et nous avons conduit deux travaux expérimentaux en mésocosmes contrôlés afin d'étudier l’effet des apports atmosphériques sur les communautés microbiennes. Ces apports ont conduit à de vrais changements dans la composition de la matière organique détectée par des méthodes spectroscopiques. Cependant, ces apports n’ont pas ou peu été utilisés pour la communauté microbienne au cours des essais expérimentaux.

En conclusion, notre étude apporte des éléments clairs quant à l'organisation et au fonctionnement des écosystèmes pélagiques méditerranéens et sur les bilans de matière à différentes échelles temporelles d’observation. De plus, le suivi mené à deux stations contrastées nous a permis de comparer la saisonnalité d'un système côtier à un système hauturier.

Mots-clés: CDOM, FDOM, MOD, déposition de poussière, biotiques, abiotiques, Méditerranée Nord-Occidentale,

ABSTRACT

The role of abiotic and biotic mechanisms controlling the dynamics of the dissolved organic matter in pelagic ecosystem (NW Mediterranean)

Chromophoric dissolved organic matter (CDOM) is a major fraction of dissolved organic matter (DOM). CDOM absorbs light over a broad range of ultraviolet (UV-R) and visible wavelengths. A small fraction of CDOM can emit fluorescence when excited by ultraviolet radiation; so called fluorescent dissolved organic matter (FDOM). CDOM plays a key role in regulating light penetration into the ocean, absorbing high-energy electromagnetic spectrum (visible and ultraviolet light) waves. On one hand, it protects aquatic organisms of potential photo-damage; in the other hand it induces a negative effect by reducing light for photosynthesis.

The optical properties of the CDOM are sensitive to biological (biotic) and physical (abiotic) processes and for this reason the colored matter can provide valuable information about the biogeochemical processes in aquatic environments. CDOM monitoring in Mediterranean coastal areas has shown different temporal trends, which go from weak to strong seasonality. Interestedly, these temporal trends were uncoupled with those of the total dissolved organic carbon. In temperate areas, episodic meteorological events can induce much more abrupt changes in the littoral than in the open sea, where changes tend to be more gradual along the year. In addition, the input of nutrients and pollutants in coastal areas is strongly influenced by the anthropogenic activity on land, and those inputs do not necessarily follow seasonal trends. In the present study, weekly and monthly samplings were performed to investigate the temporal variability in SOLA and MOLA stations, respectively. The fluctuation of different fractions of dissolved organic matter (DOM) was evaluated from February 2013 to April 2014 and referred to long time-frame databases of SOLA and MOLA stations.

Inorganic nutrients and chlorophyll shown the classical seasonal patterns, with a winter period characterized by an enrichment of surface waters favoring the spring bloom, followed by a calm period that allows the summer stratification and the depletion of nutrients in the photic zone. The stratification extended until autumn winds and low temperatures eroded the thermocline. In contrast, colored DOM fractions did not follow a clear temporal trend. Interestingly, dissolved organic carbon (DOC) exhibited the highest variability in summer, when the rest of parameters showed minimum variations. To explain this mismatch we proposed a sequence of abiotic and biotic phenomena driving the DOC dynamics. In the suggested conceptual frame, DOC dynamics depended strongly on episodic meteorological events (winds, rains, etc.) along the year, except in summer, where the biological factors were more relevant. In order to better understand the influence of biological factors, we examined the temporal trends of phytoplankton composition in relation to those of the different colored DOM fractions. We found that both phytoplankton and

CDOM were strongly influenced by abiotic factors such as the intrusions of fresh waters, the vertical mixing due to convection and the light exposure. However we did not find a correlation between any of the CDOM fractions and any of phytoplankton groups.

In addition, we use the dust deposition database of ADEPT project (ICM-CSIC, Barcelona) to investigate the potential role of atmospheric deposition in the CDOM temporal variability, and also performed two dust addition experiments with natural plankton communities collected in the Catalan coast. The experimental results shown that the dust additions induced changes in the CDOM composition, however microbes, in general, did not utilize the added compounds during the incubation period.

In summary, we provided new insights about the functioning of the Mediterranean marine ecosistems and about the temporal variability at different time scales. In addition, the monitoring study in two contrasting marine stations allowed us to compare the seasonality in a coastal system with that of offshore waters.

Keywords: CDOM, FDOM, DOM, atmospheric deposition, abiotic, biotic, Northwest Mediterranean